SAMPLING AND ANALYSIS PLAN FOR

NAVAJO NATION LAKE FISH AND WATER QUALITY MONITORING: 2003-2004

Revision 2
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Prepared for the Navajo Nation Environmental Protection Agency as part of the *Multi Media Compliance Assurance Resources for Activities in Indian Country-United States Environmental Protection Agency Project Grant* by:

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SAMPLING AND ANALYSIS PLAN FOR

NAVAJO NATION LAKE FISH AND WATER QUALITY MONITORING: 2002-2003

1.0 QUALITY ASSURANCE PROJECT PLAN (QAPP)

1.1 Introduction

The Navajo Nation Environmental Protection Agency (NNEPA) is charged with protecting the environment of the Navajo Nation. In April 1995, the Navajo Nation Council passed the Navajo Nation Environmental Policy Act, which provides guidance for NNEPA and instills Navajo philosophy regarding environmental protection. The mission of NNEPA is to protect, preserve, and enhance the environment for present and future generations, with respect to Dine values, by developing, implementing, and enforcing environmental laws; and to foster public awareness and cooperation through education.

The Navajo Nation has primary responsibility for protecting its members from the health risks of consuming contaminated fish and wildlife. One way to do this is to issue fish consumption advisories for the general population, including recreational and subsistence fishers, as well as for sensitive subpopulations (such as pregnant women, nursing mothers, and children). Fish consumption advisories are intended to inform people of high concentrations of chemical contaminants (e.g., mercury) where they have been found in local fish. Such advisories can include recommendations to limit or avoid consumption of certain fish species from specific waterbodies.

Contamination of aquatic resources, including freshwater fish, has been documented in the scientific literature for many regions of the United States (Schmitt and Brumbaugh 1990, Brumbaugh *et al.* 2001). Environmental concentrations of some pollutants have decreased over the past 25 years as a result of better water quality management practices. However, environmental concentrations of some heavy metals, pesticides, and toxic organic compounds have increased due to intensifying urbanization, atmospheric discharges, industrial development, and use of new agricultural chemicals. The Navajo Nation's waterbodies are among the ultimate repositories of pollutants released from these activities. Pollutants may come from point source discharges (e.g., industrial and municipal facilities), accidental spill events, and nonpoint sources (e.g., atmospheric deposition from various combustion and incineration processes). Once these contaminants reach surface waters, they may concentrate through aquatic food chains and bioaccumulate in fish tissues. Thus, fish tissue monitoring serves as an important indicator of water quality problems, and several states and tribes routinely conduct chemical contaminant analyses of fish tissues as part of their comprehensive water quality monitoring programs (Cunningham and Whitaker 1989). Tissue contaminant monitoring can also enable tribal agencies to detect levels of contamination in fish tissue that may be harmful to humans or wildlife.

The goal of the Navajo Nation Lake Fish and Water Quality Monitoring Project is to provide data that may be used to evaluate mercury risks to human health and bald eagles on the Navajo Nation. This data could also be used to develop site-specific bioaccumulation factors and

evaluate the need for reduced mercury emissions and discharges under the Navajo Nation Clean Water Act (NNCWA) or other authorities. This Sampling and Analysis Plan (SAP) presents the organization, objectives, functional activities, and specific quality assurance (QA) and quality control (QC) activities associated with the fish and water quality monitoring for mercury that will be conducted. The SAP also describes the specific protocols that will be followed for sampling, sample handling and storage, chain-of-custody, and laboratory analyses.

1.1.1 Purposes

The primary purposes of this study are: 1) to document the concentrations of mercury, methyl mercury, and other trace elements in fish consumed by people and wildlife; and, 2) to document the concentrations of selected trace elements in lake water of selected lakes of the Navajo Nation. Results of this study will potentially provide insight into the ecological and human health risks associated with consumption of fish from selected lakes in relation to water-chemistry conditions.

The purpose of this SAP is to ensure that data collected during the sampling program are of adequate quality to: 1) determine the fish quality in selected fishing lakes on the Navajo Nation; and, 2) to determine the concentrations of selected trace elements and mercury in lake water. The QAPP portion of the SAP (Section 1.0) describes the procedures, which will be used to document and report precision, accuracy and completeness of the analytical and environmental measurements of the lake fish- and water-quality assessment.

1.1.2 Scope

The scope of this assessment includes the collection, analysis and interpretation of surface-water and fish-quality data within selected lakes on the Navajo Nation. Four lakes known to be used either for fishing, or used by bald eagles as a prey base, were selected through consultation with the Navajo Nation Natural Heritage Program's Department of Fish and Wildlife. The actual number of lakes sampled may change due to the availability of fish species found in each lake. The proposed four lakes selected to be sampled are:

1) Wheatfields Lake (WF), coldwater lake;
2) Whiskey Lake (WL), coldwater lake;
3) Red Lake (RL), warmwater lake; and
4) Morgan Lake (ML), warmwater lake.

Samples of fish species: 1) known to be present in these lakes, and 2) known to be consumed by humans and bald eagles, will be taken. From each lake we will collect 4 composite samples of 5 fish (4 composite samples of channel catfish [*Ictalurus punctatus*] or 4 composite samples of largemouth bass [*Micropterus salmoides*] from warmwater lakes [depending on their relative availability]; and 4 rainbow trout [*Oncorhynchus mykiss*] from coldwater lakes), 3 samples of composited, filtered surface water for trace elements, and 3 samples of unfiltered surface water for mercury analyses.

All sampling activities will take place as a one-time sampling activity during March 2003, when eagles have migrated north. The analytical results should ready by September 2003. A draft final report will be ready for review in March 2004. A final report will be available for review in mid June 2004. Thirty unbound copies of the report, and thirty CD ROMs containing electronic copies of the report and raw data will be provided to the NNEPA by September 2004.

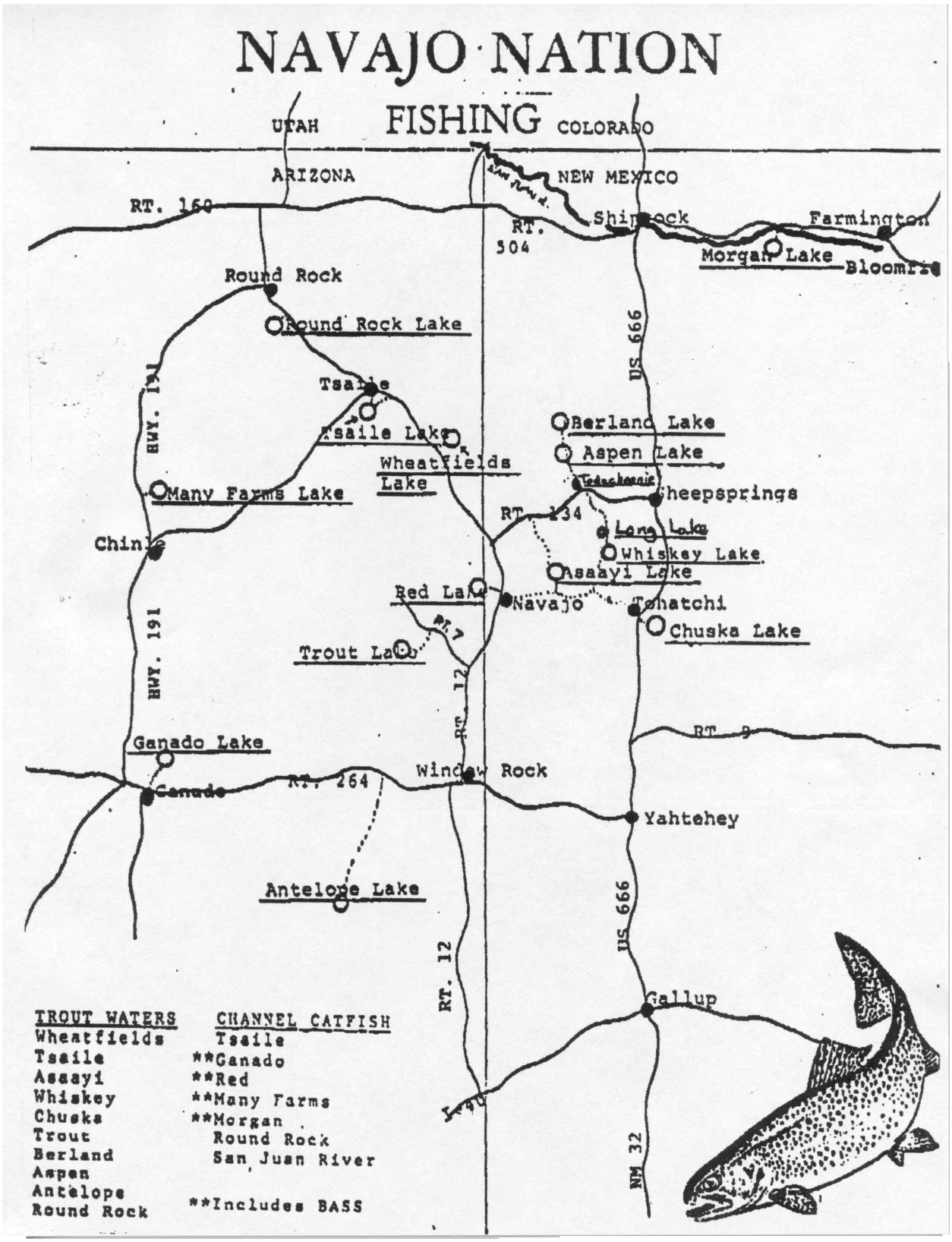

Figure 1.1.2.1.--Location of fishing lakes on the Navajo Nation.

1.2 Project Description

This project will collect requisite data for the description of trace-element contaminants in water and fish collected from selected fishing lakes on the Navajo Nation.

1.2.1 Project background

The Navajo Nation has primary responsibility for protecting its members from the health risks of consuming contaminated fish and wildlife. The Navajo Nation has proposed collecting information to determine whether to issue fish consumption advisories for the general population, including recreational and subsistence anglers, or for sensitive subpopulations (such as pregnant women and children). Such fish consumption advisories could include recommendations to limit or avoid consumption of certain fish species from specified waterbodies or, in some cases, from specific waterbody types (e.g., inland lakes, streams).

In 2002, the United States Environmental Protection Agency (USEPA; A. Strauss, Region 9, written communication) stated that it would approve the mercury criterion in the Navajo Nation Water Quality Standards (NNWQS) if the Navajo Nation adopted a human health methylmercury tissue-based criteria during the next triennial review. The Navajo Nation EPA agreed to revise the current NNWQS mercury criteria and meet the USEPA requirements.

It should be noted however, that adoption of the recommended human health criterion for mercury still may not be considered to be sufficiently protective of the potential for maternal transfer of mercury to bald eagle eggs and embryos. Developing embryos of birds are considered extremely sensitive and vulnerable to relatively minute concentrations of mercury in the egg. Scheuhammer (1987) reported that reproductive effects in birds typically occur at twenty percent of the dietary concentrations that produce lethal effects in adult birds. Therefore, the United States Fish and Wildlife Service (USFWS) and USEPA have agreed to utilize their authorities to help the Navajo Nation monitor the prey base of the bald eagle for mercury concentrations in order to allow for the development of site-specific bioaccumulation factors. Development of these factors will assist in assessing mercury exposure risk to bald eagles throughout the Navajo Nation.

1.2.2 Project objectives

The sampling program is designed to collect representative fish and water samples to accurately represent the concentrations of mercury available for consumption by anglers or bald eagles and to evaluate the water-resource conditions of selected inland fishing lakes. This SAP was written in accordance with USEPA Order 5360.1, Policy and Program Requirements to Implement the Mandatory Quality Assurance Program. In this study the USFWS will implement the fish and water sampling program to collect and analyze fish tissue and surface-water quality samples. Fish and water samples collected from four fishing lakes will be analyzed for parameters listed in Table 1.2.1.2 ***(listed metals are included as a fixed price analyte "suite")***. Laboratory analyses will be performed by the Trace Element Research Laboratory (TERL) in College Station, Texas. These fishing lakes *may* also be monitored for some or all of the following: specific conductance; pH; temperature; turbidity; and dissolved oxygen; and hardness.

Metal data, ***when applicable,*** will be compared to the cold and warm water criteria found in Table 206B.5 of the Navajo Nation Water Quality Standards (NNWQS 1999). Since many of these standards are hardness dependent, it is necessary to analyze sampled surface waters for hardness as well.

Table 1.2.1.2.— TERL method, parameter, and estimated instrument detection limit (e-IDL) for water and fish samples collected. [Critical laboratory analyses will be performed by Trace Element Research Laboratory, see Appendix A for method description. Actual method detection limits are sample dependent and will vary by sample matrix. Abbreviations: µg/L, micrograms per liter; mg/kg, milligram per kilogram; SOP; standard operating procedure, NA; not analyzed.]

Method	**Parameters**	**Sample matrix (e-IDL)**	
(See Appendix A)		**Water**	**Tissue**
TERL SOP-9030 USEPA 1638 for water samples	Inductively coupled plasma mass spectroscopy for water samples	µg/L	mg/kg
TERL SOP-9041 USEPA 200.7 for fish samples	Inductively coupled plasma atomic emission spectroscopy for fish samples		
	Aluminum	0.05	0.8
	Barium	0.01	0.4
	Boron	11	1
	Cadmium	0.01	0.04
	Chromium	0.05	0.2
	Copper	0.03	0.3
	Iron	14	4
	Magnesium	NA	4
	Manganese	0.01	0.4
	Molybdenum	0.05	1.6
	Nickel	0.02	2.4
	Lead	0.01	0.4
	Vanadium	0.02	0.1
	Zinc	0.07	0.08
TERL SOP-9050 USEPA 1631	Atomic fluorescence spectroscopy for fish and water samples		
	Arsenic	0.2	0.2
	Selenium	0.2	0.5
TERL SOP ST16 USEPA 245.5 & 245.6	Cold-vapor atomic absorption spectroscopy for fish and water samples		
USEPA 1631 for water	Mercury	***0.002***	0.02
TERL SOP 9712 for fish ***USEPA 1631 for water***	Methyl mercury	***0.0005***	0.02
USEPA 200.7	Hardness (Ca and Mg) total as calcium carbontae	1.0 mg/L	NA

This study will result in the collection of fish tissue and water-quality data in order to gain a better understanding of the conditions and fish-quality found in selected lakes on the Navajo Nation. The receptors of concern are piscivorous eagles and the fishing public. The pathways for potential contaminant release are mostly through the food web and through surface water. Only surface-water and food pathways will be investigated in this study.

1.2.3 Data quality objectives and management specifications

The *Navajo Nation Lake Fish and Water Quality Study* is not a regulatory investigation. Rather, the primary intent of data collection is to determine the current condition of fish quality in relation to surface-water resources and to provide scientists and water managers with scientific credibility in the consideration of fish consumption advisories within the area of study. Specifically, the mean concentrations of the chemicals listed in table 1.2.1.2 found in fish tissues will be compared to the USEPA screening values ***(where available),*** for consideration by the NNEPA of appropriate fish advisories. Refer to Section 1.9.4 of this document for a more detailed discussion of data interpretation.

To accomplish this, all data collected should be of adequate quality and organization to effectively communicate with respective land and water management and regulatory agencies in terms of jurisdictional authority. This requires that a broad spectrum of data analysis, management and interpretation be incorporated early in the assessment process by the USFWS and NNEPA.

Data Quality Objectives (DQOs) and measurement performance criteria for each activity in the project are addressed in this document. Primary considerations include: the intended uses of the data, type and quantity of the data, the parameters of interest (i.e. mean, range, etc.), the geographic study area, and time period. All data collection activities associated with the scheduled assessment process requires that standardized quality assurance/quality control protocol and procedures be followed. Conditions under which data are to be collected, organized and managed has been standardized and formally described utilizing provisions detailed in subsequent sections of this document.

1.3 Project Organization and Responsibilities

The NNEPA Water Quality Program and the USFWS New Mexico Ecological Services Field Office share project management and responsibilities, in accordance with a Memorandum of Agreement. These responsibilities include study design, data-collection activities, data management and interpretation activities, training, reporting, and fiscal management.

1.3.1 Responsibilities of the NNEPA Water Quality Program

The primary responsibilities of the NNEPA Water Quality Program are to: accurately define the scope and limitations of the project; identify the scenario parameters for the human health and ecological risk assessment; participate in all data-collection activities; participate in all training or presentations; provide translation or answer to members of the Navajo Nation as requested; and, co-author or provide review and comments on all interim and final reports published by the USFWS.

The Principal Investigator for the Navajo Nation Lake Fish and Water Quality Monitoring is Mr. Eric Rich, Hydrologist II, of the NNEPA Water Quality Program. Mr. Rich represents the single point of contact for all activities conducted under the Navajo Nation Lake Fish and Water

Quality Monitoring. The mission of the NNEPA Water Quality Program is to ensure the "waters of the Navajo Nation" attain, support, and maintain designated uses of these waters.

1.3.2 Responsibilities of the U.S. Fish and Wildlife Service

The primary responsibilities of the USFWS New Mexico Ecological Services Field Office are to: administer the collection and preliminary interpretation of environmental data collected during the course of the project; provide required elements of quality assurance and quality control for all data-collection activities; provide both formal and "hands-on" training to personnel of the Navajo Nation in all aspects of project implementation; interpret and report the data within the scope of the Memorandum of Agreement.

The USFWS Project Manager for the Navajo Nation Lake Fish and Water Quality Monitoring is Dr. Joy E. Nicholopoulos, Field Supervisor, of the New Mexico Ecological Services Field Office or her designee. Dr. Nicholopoulos is responsible for all project management and deliverables. The Project Officer for the Navajo Nation Lake Fish and Water Quality Monitoring is Mr. Joel D. Lusk, Senior Environmental Contaminants Biologist, of the New Mexico Ecological Services Field Office. The Project Officer will oversee all aspects of the project including: training and supervising all project team members to ensure compliance with field data- and sample-collection procedures described or cited in this document, and with field instrument calibration, operation, and maintenance procedures prescribed by the manufacturers; scheduling and ensuring collection of field quality control samples; reviewing all results of laboratory analyses; reporting verbally, through interim and draft reports, presentations, and technical reports to the NNEPA Water Quality Program on all project related matters.

Additional USFWS Field Project Leaders are Mr. James E. Brooks and Jason E. Davis, fishery biologists of the New Mexico Fishery Resources Office. Mr. Brooks and Mr. Davis are responsible for all transportation needs, provision of any necessary fish collection gear, electrofishing and boating equipment and supplies, electrofishing and boating safety, fish collection and identification, assistance with fish dissection and records, assistance with water quality measures, and coordination with the Arizona Fishery Resources Office. Mr. Lusk, Mr. Davis, other USFWS employees, volunteers, and agency personnel of the Navajo Nation will conduct all field activities.

1.3.3 Identification of subcontractors and their tasks

The New Mexico Ecological Services Field Office will contract laboratory services through the USFWS Patuxent Analytical Control Facility (PACF). The PACF is a USFWS Field Station of the Division of Environmental Quality located at the Patuxent Wildlife Research Center in Laurel, Maryland. The contact at PACF is Mr. John Moore (301-497-5680). The PACF provides analytical chemistry services to the USFWS. The PACF maintains the Environmental Contaminants Data Management System (ECDMS), a database that stores sample collection and analytical data. The PACF establishes and maintains contracts with several laboratories. The USFWS will provide PACF with a catalog, through the ECDMS, which describes the samples to be analyzed, the analyses requested, and the cost code from which funds will be used for payment. The PACF selects the contract laboratory for analyses, handles the procurement, and

authorizes the client to ship the samples. Upon completion of the analysis, the contract laboratory sends the analytical report to PACF; it is reviewed by the PACF Quality Assurance Team for conformance to the PACF QA Criteria. If the report is acceptable, the results are sent to the client. Problems are referred back to the contract laboratory for corrective action. Catalogs submitted through ECDMS are electronically reported to the client and the data are stored in the database. The PACF will be responsible for assuring the quality of the chemical analyses it provides through the contract laboratory, Trace Element Research Laboratory. The quality of a chemical analysis is considered assured when the analysis is performed in a technically competent manner, by qualified personnel using appropriate methods and equipment, and the precision and accuracy of the measurement are within the expected ranges for the technique.

Contact information for contract laboratory services is:

Mr. Robert Taylor, PhD.
Trace Element Research Laboratory (TERL)
Texas A&M Research Foundation - Department of Oceanography
100 Bizzell Street
Eller Building, Room 403
College Station, TX 77843-3146
(979) 845-9442

Descriptions of the processes used to evaluate this laboratory's capability are included in Appendices A and B. Should the analytical services of the TERL be of inadequate quality or prompt in the analysis, the USFWS will identify an alternative analytical laboratory.

1.3.4 Project Fiscal Information

The NNEPA has prepared an application for a grant totaling $53,000.00 offered by the USEPA in order to evaluate the need for fish consumption advisories on waters of the Navajo Nation. Under a Memorandum of Agreement, the Navajo Nation would contract with the USFWS to conduct the Navajo Nation Lake Fish and Water Quality Monitoring Project. Anticipated project costs are:

USFWS Personnel (including number of staff days)		
NMES Contaminant Biologist (20 days @ $650 per day)	$13,000.00	
Fishery Resource Offices (8 days @ $250 per day)	$6,000.00	
Subtotal		$19,000.00
Travel/Per Diem		
8 trips (scoping, field work, and presentations)	$3,000.00	
Subtotal		$3,000.00
Laboratory Services (TERL)		
Water Analyses ($407 each)	$7,333.00	
Fish Tissue Analyses ($676 each)	$9,390.00	
		$16,123.00
Equipment and Supplies		
Equipment (bottles, churns, bottles, foil, etc.)	$3,000.00	
Supplies (buffers, standards, shipping, etc.)	$1,277.00	
Subtotal		$4,277.00
Administrative Overhead (20 %)		$10,600.00
GRAND TOTAL		$53,000.00

1.4 Quality Assurance Objectives for Measurement Data

The objective of the project QAPP is to monitor the overall program for all environmentally related data collection and analyses to ensure that all data generated are suitable for evaluation and interpretation of fish tissue and water quality at the fishing lakes. The QAPP is divided into two major parts; overall program quality assurance/quality control (QA/QC) and laboratory QA/QC. Oversight of the overall program QA/QC is the responsibility of the Project Officer. Laboratory QA/QC is the responsibility of the PACF and TERL QA/QC manager. This section defines the recommended QA objectives or goals for accuracy, precision, completeness, representativeness, and comparability. These goals present the acceptable standards that field

and laboratory teams must plan to meet before sampling begins. Because the effectiveness of a quality assurance program generally is measured by the quality of data generated by the laboratory, much of what is presented in this SAP applies to laboratory operations, although, specific procedures to be used in the field are also described.

Quality assurance will be emphasized and carried out conscientiously by following procedures in this SAP that will prevent the introduction of contaminants into fish and water samples and that will chemically stabilize any samples before laboratory analyses. Additionally, field instruments will be calibrated frequently and checked against concentration standards. Laboratory data will be examined relative to QA/QC sampled data. All laboratory detection limits are sufficient and less than screen levels.

1.4.1. Definition of Criteria

The effectiveness of a QA program is measured by the quality of data generated. Data quality is judged in terms of its accuracy, precision, completeness, representativeness, and comparability. These terms are described as follows:

Accuracy - the degree of agreement of a measurement with an accepted reference or true value, usually expressed as the difference between the two values, or the difference as a percentage of the reference or true value. Accuracy is a measure of the bias in a system.

For the field measurements, with the exception of location, the true value is dependent on the calibration of the instrument (ruler or scale). Following calibration procedures and precision requirements will provide an indication of accuracy. Following SOPs as written should reduce contamination as much as possible. Accuracy is also based on training. Accuracy of field measurements will be evaluated by:

a) standard methods - methods of measurement shall be used which, whenever possible, are recognized and considered as standard by the scientific community.

b) calibration and calibration checks of field instruments and equipment shall be performed at a frequency that will insure measurement is accurate.

c) collection of field blanks for water analyses.

Accuracy of laboratory analytical data will be evaluated by:

a) standard methods - methods of measurement shall be used which, whenever possible, are recognized and considered as standard by the scientific community. USEPA methods, generally, shall be used.

b) calibration standards - primary standards shall be obtained from NIST (National Institute of Standards and Technology) USEPA repository, or other reliable commercial sources.

c) surrogate spikes - recovery of organic surrogate analytes shall be within three standard deviations of the laboratory-established average recovery of the surrogate analyte.

d) known laboratory control samples - recovery of analytes shall be within three standard deviations of the laboratory-established average recovery of the analyte, not to exceed the range specified by the SW-846 methods. For multi-analyte method, 95 percent of the analytes must be within control limits.

e) frequency that will insure measurement is accurate.

The determination of the accuracy of a measurement requires knowledge of the true or accepted value for the signal being measured Accuracy may be calculated in terms of percent recovery as follows:

$$Percent\ recovery \equiv \frac{X}{T} \times 100$$

where: X = the observed value of measurement
T = "true" value

Precision - the degree to which the measurement is reproducible. Precision is a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Another term for precision is repeatability. Repeatability in the field is very important to precision, as well as data comparability. Repeatability is controlled by the development of detailed SOPs and adequate training in those SOPS. Field precision will be checked by remeasuring 10% of the samples. Precision is best expressed in terms of the standard deviation. Standard deviation (S) is calculated as follows:

$$S \equiv \frac{1}{n-1} \sum_{i-1}^{n} \left(x_i - \overline{x} \right)^2$$

where a quantity "x" (e.g., a concentration) is measured "n" times.

Precision of laboratory analytical data will be evaluated by:

a) duplicate control samples (DCS) - replicate analyses of analytes shall be within laboratory established control limits.

b) matrix spike duplicates - agreement between duplicate analyses of inorganic spiked analytes shall be within the relative percent difference (RPD) limits specified in SW 846, Third Edition (USEPA 1986a) unless otherwise specified.

In the case of duplicates, the RPD between the two samples may be used to estimate precision.

$$RPD \equiv \left| \frac{D_1 - D_c}{(D_1 + D_c)/2} \right| \times 100$$

where: RPD = relative percent difference
D_1 = first sample value
D_2 = second sample value (duplicate)

Completeness - a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. In the field, completeness is defined as the successful collection of all viable samples in the appropriate time frame. A viable sample would be defined as any single sample whose integrity has not been affected during the collection process and would therefore not be flagged with a field qualifier.

The DQOs are based on the evaluation of a statistically relevant number of samples, which are affected by all errors occurring in the field and laboratory. Therefore, the overall ***goal*** is a completeness of 95***%. The goal will be to have*** at least 95 percent of the laboratory analytical batches associated with acceptable QC results. ***The goal will aslo be to have*** at least 95 percent of the laboratory analytical methods in control and at least 95 percent of the analytes in control for a method to be in control.

The percent completeness for each set of samples is calculated as follows:

$$Completeness = \frac{valid\ data\ obtained}{total\ data\ planned} \times 100$$

Completeness of field data will be evaluated by:

a) all measurements and observations shall be recorded on logsheets in a notebook and reviewed in terms of stated goals.

b) all deviations from the SOPs shall be recorded and documented.

Completeness of laboratory analytical data will be evaluated by:

a) each data set (batch) shall contain all QC check analyses verifying precision and accuracy for the analytical protocol and shall be reviewed in terms of stated goals.

b) each data set (batch) shall contain all field and trip blank analyses.

c) all pertinent dates are recorded (dates received, extracted, analyzed, etc.).

d) all requested analyses shall be performed or documentation provided as to the reason for nonperformance.

Representativeness - the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Representativeness of field data will be evaluated by:

a) use of standard methods of measurement and sample collection.

b) collection of sufficient size or amount of sample.

c) documentation of reasons for use of nonstandard techniques.

d) adherence to chain-of-custody procedures.

Representativeness of laboratory analytical data will be evaluated by:

a) use of preservation techniques (including chilling during shipment) to minimize sample degradation which may occur between sample collection and sample analysis.

b) holding times prescribed by 40 CFR 136 shall be adhered to by the analytical laboratory.

c) field and laboratory blank analyses will be used to determine if samples have been contaminated.

Comparability - express the confidence with which one data set can be compared to another using the same property. Comparability will be maintained by the adherence to the SOPs. Adherence to these SOPs by all samplers will allow for comparability of data among sites and throughout the project.

Comparability of field measurements will be evaluated by:

a) standard methods - methods of measurement shall be used which, whenever possible, are recognized and considered as standard by the scientific community.

b) reporting units - data shall be consistently reported in units recognized and considered as standard by the scientific community.

Comparability of laboratory analytical data will be evaluated by:

a) standard methods - methods of analysis shall be used which are recognized and considered as standard by the scientific community. USEPA methods are generally used.

b) reporting units - data shall be consistently reported in units recognized and considered standard by the scientific community.

c) the use of traceable materials for calibration and quality control.

1.4.2 Goals

The numerical QA goals for measured data are as follows:

	PARAMETER	ACCURACY	PRECISION	COMPLETENESS
1	Analytes (laboratory) in water or fish	+ or - 3 standard deviations (sigmas) of known standard concentrations	RPD within laboratory determined control limits	95%

Failure to achieve these criteria shall require additional analysis or other agreed upon action.

1.4.3 Second Order Data

Second order data is defined as information and/or data acquired from any source outside of the USFWS study described in this SAP that may impact the environmental decision making process (i.e. where to sample, what to sample for). Second order data may include literature reviews and historical data assembled by the USFWS relevant to the assessment, as well as other data collected during the study by other Federal, Tribal, State or other entities.

Examples of second order data may include the following:

- Fish stocking records;
- Limnological surveys of these lakes;
- Maps or aerial photographs of lakes depicting wetlands;
- Reports of piscivorous bird usage;
- Computer databases;
- Numerical simulations (models);
- Spreadsheets and programs;
- Literature; and
- Other sampling events (i.e. historical data collected by USFWS prior to this study).

Issues that shall be addressed when using second order data include, but are not limited to the following:

- Source of the generated data;
- How the data will be used (i.e., what decisions affecting data quality will be made based upon the data); and
- The quality of the data;

- If the data were generated under an approved QAPP or other appropriate sampling document, this will be stated and the document will be referenced by title, date, preparing organization, and approving organization;
- If the quality of the data is unknown or uncertain, this will be stated and any limitations on the use of the data will be indicated; and
- If the data are obtained from the only available source, this will be stated, a description of any information known or not known about the quality of the data will be included, and any limitations on the use of the data will be indicated.

When using second order data, all available detail regarding the data will be provided to allow the user of this information to understand how it was determined that the acquired data is acceptable for use in decision making. In determining if the data are acceptable, the following information will be considered:

- representativeness of the data;
- bias;
- precision; and
- qualifiers associated with the data.

1.5 Sampling Procedures

Standardized sampling, handling, and analysis procedures will be followed Documented procedures/protocols are identified in the following sections.

1.5.1. Sampling protocols

Specific sampling procedures that will be followed for the collection of fish and water samples are described in Section 2.0 of this SAP. General sampling procedures follow methods described in the technical documents referenced in Section 3.0 of this SAP.

1.5.2. Sampling handling

The required sample volume, preservation, and analytical holding times by method for fish and water samples are presented in Table 1.5.2.1.

Table 1**.5.2.1. Sample type, preparation, containers, holding times, and analyses.**

Sample Type	Preparation	Preservative	Container	Holding Time	Analysis
Fish	length and weight measured, spines removed	cold/frozen	plastic bags	6 months	trace elements
Fish fillet	skin removed and weight measured	cold/frozen	500 mL, chemically clean glass jar	1 month	methyl mercury, trace elements
Water	filtered though inline 0.45 µm	prepreserved ultra pure HNO3	500 mL, Nalgene jar	6 months	trace elements
Water	clean hands / dirty hands	prepreserved Omni Trace 1 % HCl	1 L, rigorously cleaned, Teflon container	1 month	methyl mercury
Water	none	none	none	none	field measurements
Water	none	prepreserved HNO3	500 ml, Poly	6 months	hardness

1.6 Sample Custody

1.6.1 Field operations

Sample handling and custody procedures for the field investigation will be discussed in sections 2.2.2 and 2.2.3 of the field sampling plan (section 2.0 of this document).

1.6.2 Laboratory operations

Laboratory procedures for sample handling, sample identification and sample custody are discussed in the following subsections.

1.6.2.1 Sampling handling and custody

Samples received by the laboratory are carefully checked for label identification, chain-of-custody, and any discrepancies. Photographs document the condition of samples and each sample is then assigned a unique laboratory identification number, which stores all identifications and essential information. These internal chain-of-custody procedures track the sample from storage through the laboratory system until the analytical process is complete and

the sample is submitted for disposal or returned to the client. Access to the laboratory is restricted to prevent any unauthorized contact with samples, extracts or documentation.

1.6.2.2 Sample identification

Each sample collected is uniquely identified by an six digit alphanumeric sample identification number. The field number, whether a water or fish sample, is assigned by the USFWS Project Officer. This number is unique in that it applies specifically to a given sample site and to no other. The number usually is assigned when a sampling site is first established and is retained for that sampling site indefinitely. The first two digits denote the site initials; the next two digits denote the sample type; and the last two digits (assigned sequentially) uniquely identify the sample number. Samples are further uniquely identified by their weight and date they were collected. Field blank and duplicate water samples will also be uniquely identified by a field sample identification number.

1.7 Calibration Procedures and Frequency for Field Test Equipment

Field measurement of water quality conditions are non critical. However, field equipment calibration procedures and frequency are discussed in Section 2.3.2 of the Field Sampling Plan (Section 2.0 of this document).

1.8 Analytical Procedures

1.8.1 Identification of methods

Methyl mercury in fish samples will be analyzed by cold vapor atomic absorption spectroscopy. Remaining trace elements in fish and water samples will be analyzed by the methods detailed in Table 1.2.1.2 and Appendix A.

1.8.2 Analytical detection limits and quality control

The sensitivity of an analytical method is related to the detection limit which is the lowest concentration of an analyte that can be detected at a specific confidence level (detection levels are listed in Table 1.2.1.2). Quality control samples will be processed in a manner identical to actual samples, and include reagent blanks, spiked blanks, duplicates, and spiked samples. Blank levels will be no more than 2x method detection limit (MDL). If blank levels for any analyte are above the 2x MDL, samples analyzed in that sample set should be reprocessed after the source of contamination is isolated. At least one reagent blank is analyzed with each batch of samples. Percent recovery of the spike is calculated and used as a measure of accuracy. Matrix spikes are used to investigate possible interferences that may result in either signal enhancement or suppression. Samples are spiked with methylmercury at levels higher than expected. Matrix spikes consist of at least 5% of the number of samples analyzed. An inorganic mercury spike may be included to demonstrate that inorganic mercury species are not extracted along with the methylmercury fraction. Duplicate samples are run with every 20 samples or with every sample set. Certified reference materials samples are run with every sample set. Percent recovery of the certified value is calculated and used as a measure of accuracy.

1.9 Data Reduction, Validation, and Reporting/Interpretation

1.9.1 Data Management

The project's overall data management will move along the steps outlined below. The person, or laboratory, responsible for each step is listed. The Project Office will delegate authority and responsibility for satisfactory completion of the data management steps under his or her supervision. Any corrections required will be returned to earlier steps. The data management steps are as follows:

	DATA MANAGEMENT STEP	**BY**
1.	Daily logbook entries and data collection schedule	Collector
2.	Field measurements and forms	Collector
3.	Sample collection and forms	Collector
4.	Daily QA/QC on-site review of field logbooks, measurements, and sample collection forms	Field Team
5.	Sample processing and shipment	Collector
6.	Monthly QA/QC on-site review of field logbooks, measurements and sample collections	Project Officer
7.	Laboratory analyses	TERL
8.	Laboratory reports of results and QA/QC data	TERL
9.	Laboratory reports review	PACF
10.	Data check and validation	Project Officer
11.	Data compilation and check against Tribal standards	Project Officer
12.	Data collection progress review/report	Project Officer
13.	Data incorporation into final report	Project Officer
14.	Review and approval of final report	Field Supervisor Principal Investigator

1.9.2 Data reduction

Data produced by all field and laboratory activities will be reduced (generally to tabular form), checked for accuracy by the field personnel or laboratory analyst and a reviewer, and reported in computerized and hard copy formats. Data produced by field activities will be recorded in bound notebooks. Raw data resulting from analytical procedures are reduced to reported concentrations by the analyst following guidance and equations in the appropriate USEPA or approved method.

1.9.3 Data quality assessment

The field team performing field measurements has the prime responsibility for entering data and observations into field notebooks or field logsheets. Each page will be initiated by the person recording the information. Another team member, on site, will inspect the entries for accuracy and adherence to standard procedures or documentation for nonstandard procedures. The Project Officer or her designee will periodically review field notebooks for completeness and adherence

to standard procedures. The Project Officer or her designee will review all data prior to entry into a computer database to ensure that standard procedures were followed, all QA/QC checks were performed, anomalies were documented, and data packages are complete.

Three levels of review are performed in the laboratory. At level 1, the laboratory chemist generating the data has the prime responsibility for the correctness and completeness of the data. Each analyst reviews a data package to ensure that: (1) sample preparation information is correct and complete; (2) analysis information is correct and complete; (3) the appropriate standard operating procedures have been followed; (4) analytical results are correct and complete; (5) samples are within established control limits; (6) blanks are within appropriate QC limits; (7) special sample preparation and analytical requirements have been met; (8) documentation is complete (e.g. all anomalies have been reported, holding times have been reported, etc.); and, (9) all calculations have been checked.

At level 2, an independent review of laboratory data is performed by laboratory personnel to ensure that: (1) calibration data are scientifically sound, appropriate to the method, and completely documented; (2) QC samples are within established guidelines; (3) qualitative identification of sample components is correct; (4) documentation is complete and correct; (5) data are ready for incorporation into the final report; and, (6) data package is complete and ready for data archives.

At level 3, the laboratory program manager reviews the report to ensure the data meet the overall objectives of the PACF and USFWS.

All laboratory results will be reviewed by both the laboratory and PACF personnel. This review will focus on the following:

Chain-of-custody forms.
Holding times.
Method calibration limits.
Method blanks.
Laboratory-established detection and quantitation limits.
Analytical batch control records, including spike recoveries and duplicate results.
Corrective actions.
Formulas used for analyte quantitation.
Calculations supporting analyte quantitation.
Completeness of data.

The established detection, quantitation, and control limits will be verified. Method validation will ensure that control charts and statistical calculations are updated to include recent data. Any trends or problems will be noted by the project chemist and any laboratory-established detection or quantitation limits that exceed those in this SAP will be identified. Excessive holding times will be noted. Method calibration and instrument calibration will be verified to assure that no project samples were analyzed when instruments were not properly calibrated.

Environmental sample data will be compared to quality control data to ensure accurate and validated data. This determination will be made using the professional judgment of a multidisciplinary team of hydrologists, biologists, chemists, quality assurance officers, and other personnel having direct experience with the data collection effort. Field duplicate results, field and laboratory blank results and sample matrix effects will be evaluated to identify valid data. Environmental data that are not representative of environmental conditions or were generated through poor field or laboratory practices shall not be used in the evaluation process.

Results from the analysis of blanks will be assessed to determine the sources of contamination and the impact of any contamination on the analytical results for environmental samples.

Contamination proven to be a constant, low-level systematic error that cannot be eliminated will be noted in the interim report, and its impact on the analytical results for environmental samples will be evaluated. The results for environmental samples will not be "corrected" for blank contamination.

1.9.4 Reporting and data interpretation

Field and laboratory data will be provided to Navajo Nation in an interim and a draft final project report, informal technical information reports, data-validation reports, and upon written approval, in a final technical report. Laboratory data and some field data will also be provided in a computerized format compatible to Microsoft software. Quality will be assured during data validation and technical report preparation. The Project Officer or delegated staff will check for the following:

Completeness of field records.
Identification of valid samples.
Correlation of field test data.
Identification of anomalous field test data.
Accuracy and precision of the field test data and measurements.

Field records will be checked to assure that activities required have been accomplished and that field documentation ensures sample integrity and provides sufficient technical information to re-create each field event. Completeness checks will be documented, and environmental data affected by incomplete records will be identified in the documentation.

Identification of valid samples will involve interpretation and evaluation of the field records to detect problems affecting the representativeness of environmental samples. Judgments of sample validity will be documented in a data-validation report and environmental data associated with poor or incorrect field work will be identified in that report.

Field test data will be correlated to assure that data collected by various methods are interpreted consistently. Findings of these correlations will be reported. Anomalous data will be identified and discussed. As requested, an amendment to the Memorandum of Agreement can provide for confidentiality of proprietary, inconclusive, or unsubstantiated information.

Data Treatment and Statistics

Some environmental data will be received in an electronic format. Other data will be initially recorded by hand on printed data forms or notebooks in the field, then transferred to electronic format as spreadsheet data. Printed data sheets and electronic data spreadsheets will be compared to verify accuracy of transfer. Some of the environmental contaminant data will be reported in either dry weight (DW) or wet weight (WW) concentrations and will be so indicated. For statistical purposes and simplicity, all results that are below the analytical laboratory's instrument detection limit, will be replaced with a value one-half the instrument's detection limit prior to further statistical treatment as per USEPA (1998b). Some data will be natural log-transformed to normalize the data distribution prior to parametric statistical tests (Bailey 1981) such as the one-way analysis of variance or students' t-test. Nonparametric statistical tests may also be employed and will be so indicated in text. Several descriptive statistics and analyses (*e.g.*, regression, principal component analyses) will also be conducted on concentrations of selected contaminants in fish tissues. Unless otherwise specified, statistical significance will refer to the level of $p < 0.05$. In addition to spreadsheet software programs, the program STATISTICA (StatSoft Inc. 1994) will be used for statistical summaries and testing of data.

Water Quality Evaluation Methods

Identification of contaminants of concern in surface waters collected for the Navajo Nation Lake Fish and Water Quality Monitoring will be accomplished on a lake basis (*i.e.*, the three collection sites on the lake will be averaged). The process will begin with examination of the existing water quality data for compatibility with approved collection, storage, and analytical methods. The major evaluation method will include a comparison of the concentrations of chemicals in the water column to the various water quality criteria for the beneficial uses of surface waters in the Navajo Nation (NNWQS 1999). As necessary, the water quality standard will be computing using the functional relationships of hardness and other factors as they affect the water quality criteria. When the contamination of field blanks or laboratory blanks is and it was above or approached the water quality criterion, ***then these data will be reported with a data qualifier.***

Fish Tissue Quality Evaluation Methods

Identification of contaminants of concern in whole body fish collected for the Navajo Nation Lake Fish and Water Quality Monitoring will be accomplished on a species and lake basis. The evaluation methods included a comparison of the concentrations of chemicals in fish tissues to a reference site (tentatively Wheatfield Lake) as well as to various concentrations (Tissue Quality Criteria) reported in the literature that affect wildlife or livestock (NRC 1980; Sample *et al.* 1996; USDOI 1998). For whole body fish, mean concentrations reported in the re-integrated fish will be compared to concentrations in whole body fish collected nationwide (Schmitt *et al.* 1999), to threshold concentrations in fish fillets consumed by people (USEPA 1997a), and in fish fillets collected regionally (Fresquez *et al.* 1999; Simpson *et al.*). Emphasis was placed on the bioaccumulation of contaminants that are known to pose serious health risks to wildlife or

people. ***Both water and fish quality data will be used to assist in fish advisory program development.***

After fish dry weight concentrations have been converted to wet weight, all fish which had fillets removed and corresponding partial body samples submitted for analysis will be "integrated" (as the sum of weighted concentrations of the parts of a fish) to yield "whole" fish analytical concentrations. This allows comparisons with other whole body samples as well as with other studies, which reported whole body sample contaminant residues. This also allows the direct comparison between fillet concentration and whole body concentration. An example of the "integrated-fish" calculation method is provided below. If a particular analyte concentration is below the detection limit in the fillet but not in the partial body, then a value of one-half the detection limit concentration will be assigned during the calculation of the integrated-fish concentration. If both the fillet sample and partial-body sample have an analyte concentration that was below the detection limit, then the higher of the two detection limits, preceded by a "less than" symbol (<), will be presented in the data tables as the integrated-fish concentration.

Integrated fish concentration = [(fM/wM) x cF] + [(pM/wM) x cP]

where:

fM = mass of a fillet (g)
wM = whole body mass = mass of fillet + mass of partial body (g)
cF = contaminant concentration in a fillet (mg/kg)
pM = mass of partial body (g)
cP = contaminant concentration in partial body (mg/kg)

example:

Given:
fM = 20 g
pM = 180 g
wM = fM + pM = 200 g
cF = 0.5 mg/kg
cP = 2.8 mg/kg

Then:
integrated fish concentration =

((20g/200g) x 0.5mg/kg) + ((180g/200g) x 2.8mg/kg)

= 2.57 mg/kg

WILDLIFE AND HUMAN HEALTH RISK ASSESSMENT

Trace element concentrations found in trout or catfish may be used to evaluate the potential risk to wildlife or humans consuming fish from the Navajo Nation Lakes as requested and provided with appropriate scenarios of exposure by the Environmental Protection Agency Water Quality Program. Several potential human exposure pathways could be considered (Table 1). One scenario could be of a child, age 1 to 6, that would consume up to 0.085 kg (~3 ounces) of fish per day for up to 156 days out of the year (3 times/week). This scenario is believed to be a reasonable risk assessment of the human consumption of fish from the Navajo Nation Lakes, as children are believed to be sensitive of contaminant-related risks.

This risk assessment, however, will not necessarily provide a complete picture of contaminant-related risk at these fishing lakes. It will be based on a relatively small number of fish samples, and should be viewed as a preliminary screening of potential risk. Furthermore, any risk assessment makes assumptions and can not take into account those site-specific factors that may deviate from the norm, such as daily fishing and consumption of fish, additional ingestion of water and sediment from recreational use, or irregular fishing patterns. This risk assessment will assume "average" conditions and will not take into account such factors as the bioavailability of contaminants or any special method of food preparation.

Table 1. Summary of parameters for estimating daily intake of trace elements in humans

Subpopulation	Fish Ingestion Rate (kg/day)[a]	Exposure Frequency (days/year)[b]	Body Mass (kg)[a]
ages 1 - 6	0.085	14	14.5
ages 1 - 6	0.085	156	14.5
adults	0.114	14	70.0
adults	0.114	156	70.0

a Based on USEPA (2000) suggested "meal sizes" and typical body weights.
b Estimates for recreational fishing = 14 days/yr, and subsistence fishing = 156 days/year (3 days/week). These assumptions are *not* based on actual surveys of fishing patterns at the Navajo Nation Lakes.

Estimates of risks to human consumers of fish will be evaluated according to USEPA (1999) and other published data ***where such data is available for individual contaminants***. Contaminant concentrations used to estimate daily intake values will be obtained from the mean concentration or 85th percentile concentration of each of the elements used in the risk assessment. For human health considerations, only fillets were to be considered consumed from fish. Once the contaminant intake rate is calculated, it will be divided by USEPA oral ingestion related risk Reference Doses (RfDs) to obtain a Hazard Quotient (HQ). RfDs will be obtained from chronic daily intake levels above which adverse health effects are suggested may occur. An RfD is a concentration at which humans are unlikely to experience an appreciable risk of noncarcinogenic deleterious effects over a lifetime. Inherent in the RfDs are uncertainty factors. An uncertainty factor of 10 has been calculated into the RfD values derived from the USEPA No Observed Adverse Effect Level (NOAEL) for individual elements to account for variation between animals studied in the laboratory and the human population.

The calculation of potential human daily intakes of trace elements due to fish ingestion will be calculated according to the following formula:

Equation B-1. Equation used to estimate daily contaminant intakes due to ingestion of fish items.

$$Intake = (C_m \times SFIR \times EF)/(BW \times AT)$$ where:

Intake	contaminant intake rate (mg/kg-day)
C_m	contaminant m concentration in fish (mg/kg)
SFIR	subpopulation (e.g., adults vs. children) fish ingestion rate (kg/day)
EF	exposure frequency (days/year)
BW	body mass (kg)
AT	averaging time (days/year)

Another factor of 10 was used by the USEPA if the value was based on the Lowest Observed Adverse Effect Level (LOAEL). An additional factor of 10 was added to account for sensitive subpopulations, such as children, pregnant women, or smaller than average adults. The RfDs for the elements used in this risk assessment are listed below in Table C-2.

Table C-2. Oral reference doses for elements used in the risk assessment and reference.

Element	Oral RfD (mg/kg-day)	Reference
Arsenic	0.0003	IRIS
Cadmium	0.0005	IRIS
Copper	0.0371	HEAST
Mercury	0.0003	IRIS
Selenium	0.005	IRIS
Zinc	0.3	IRIS

HEAST -- USEPA Health Effects Assessment Summary Tables, 1992
IRIS -- USEPA Integrated Risk Information Service, 2001

Based on these data, a hazard quotient will be calculated for each element ***for which these data exist***. If the HQ obtained is above one, then risk associated with the consumption of fish will be considered to be elevated. To obtain the hazard quotient, one obtains an individual characterization of risk for each element. These individual characterizations can be excellent indicators of potential contaminant-related problems, but do not adequately express the combined risk from all elements in the fillets. Therefore, from these individual element HQs, an aggregate Hazard Index (HI) will be obtained, which shows the combined effect of contaminants, by adding together the individual element hazard quotients. If a hazard index is less than one, chronic adverse effects from ingestion of fish will be considered unlikely to occur. The hazard index assumes that a threshold exists (i.e., HI $\geq$ 1) below which exposure does not cause adverse effects. The hazard index that will be used here assumes elements act additively, and it does not take into account synergistic or antagonistic interactions between elements, or other more complex biological processes, such as organ transport. Hazard indices and hazard quotients for adult and children fishers will be calculated and presented in the data tables. A preliminary risk characterization will be provided in the interim report, and if requested in the final report. The risk characterization should be considered as preliminary, as it was only applied to average or assumed scenarios (ultimately, worst case). Creel surveys, and other methods to quantify actual fish consumption rates, may be necessary to confirm any assumptions of fish consumption rates used in these calculations.

For the bald eagle (and other representative piscivorous species), fish are the primary prey. Therefore, health risks from contaminants in fish from the Navajo Nation fishing lakes will be evaluated by comparing mean, 85th percentile, and maximum metal concentrations in fish tissues to published ***and known*** Toxicity Reference Values (TRVs) for adverse health effects in similar surrogate species (Table 3; USEPA 1998b). Food consumption rates and bird body weights will be derived from the USEPA Wildlife Exposure Handbook. Assuming a "worst-case scenario" in which exposure duration is 365 days/year and 100 percent fish consumption, a contaminant intake rate will be calculated, and expressed as mg/kg/day.

Dividing the contaminant intake rate by the TRV will yield a Hazard Quotient (HQ), where a HQ greater than 1.0 indicates a potential risk to that organism (see Equation 2). The HQ is an individual characterization of risk for a particular element. From these individual element HQs, an aggregate Hazard Index (HI) will be obtained, which will show the combined effect of contaminants, by adding together the individual element hazard quotients. If a HI is less than one, chronic adverse effects from ingestion of fish will be considered unlikely to occur. The HI assumes that a threshold exists (i.e., HI greater than or equal to 1) below which exposure does not cause adverse effects. The HI used here assumes elements act additively, and does not take into account synergistic or antagonistic interactions between elements, or other more complex biological processes, such as organ transport. All hazard indices and hazard quotients for wildlife consumers will be calculated and presented in data tables. A preliminary risk characterization will be provided in the interim report, and if requested in the final report.

Equation 2. Equation used to estimate daily contaminant intakes due to ingestion of fish.

$$Intake = (C_m \times FDIET \times EF)/ (BW \times AT)$$

where:

Intake	contaminant intake rate (mg/kg-day)
C_m	contaminant m concentration in fish (mg/kg)
FDIET	Fraction fish ingestion (0 - 1)
EF	exposure frequency (days/year)
BW	body mass (kg)
AT	averaging time (days/year) - 365

Table 3. Toxicity Reference Values (TRVs) for elements used in risk assessment calculations and reference.

Element	TRV (mg/kg-day)	Reference
Arsenic (total)	5.140	Sample *et al.* 1996
Cadmium	1.450	Sample *et al.* 1996
Chromium (VI)	1.000	Sample *et al.* 1996
Copper	28.000	Chino ERA 1999
Lead	0.450	Sample *et al.* 1996
Mercury	1.130	Sample *et al.* 1996
Selenium	0.500	Sample *et al.* 1996
Vanadium	2.400	Chino ERA 1999
Zinc	14.500	Sample *et al.* 1996

2.0 FIELD SAMPLING PLAN (FSP)

The scope of the Navajo Nation Lake Fish and Water Quality project consists of fish and water collection, preparation, analysis, and data evaluation. Addition water quality measurements of dissolved oxygen, temperature, specific conductivity, and pH will be taken to characterize the aquatic environment. The following sections provide an overview of the field sampling plan, requirements and procedures for field methodologies to be employed, field QA/QC program, and reporting of field measurements and analytical results.

2.1 Field Operations

2.1.1 Surface-water sampling

Surface-water will be sampled at 15 locations along 2 perpendicular cross-sections in each lake accessed by a boat and composited into 3 water samples for analyses. Sampling locations will be distributed equidistant along the perpendicular cross-sections, with 10 locations along the longest cross-section composited into 2 water samples, and 5 locations along the shortest cross-section

composited into 1 sample. Surface water samples will be collected from the top of the water column. A Teflon, DH-95 surface-water sampler, bottle, cap, and nozzle will be used to collect the water sample. Surface-water samples to be analyzed for trace elements will be transferred from the plastic bottle and composited ***(lower precision required)*** in a plastic churn splitter. The composited water will then be transferred from the sample churn using a peristaltic pump, C-flex tubing, and a 0.45 micron in-line capsule filter to the sample bottle. However, samples to be analyzed for methyl mercury concentrations will be grab ***(higher precision required)*** samples transferred directly to sample bottles. In total, 3 grab samples for methyl mercury analysis and 3 filtered samples composited from 5 locations will be collected.

Water sampling of the lakes will occur by boat. A line of the shortest traverse from entry to the opposite shore will be travelled by boat. At approximately equi-distant points along that line the boat will cease movement 5 times and 2 liters of water will be collected from the epilimnion for compositing. At one location along the traverse, grab samples will be collected, using ultra-clean techniques, for mercury and methyl mercury analyses. Next we will travel along a line of longest traverse that is perpendicular to the first traverse line. At approximately 5 equi-distant points along the first half of that line the boat will cease movement and 2 liter samples of water for compositing will be collected from the epilimnion. This practice will be repeated on the second half of this perpendicular traverse. This will result in 3 composited water samples for a metal scan, 3 grab samples for a mercury scan, and 3 grab samples for a methyl mercury scan for each lake. While lake water quality is known to have spatial variability vertically, horizontally, and seasonally, the sampling design cannot accomodate these factors within the budget.

Field quality control samples will be obtained. Field duplicates will be obtained at a frequency of 10% of all samples. One equipment blank will be obtained during sampling. The laboratory will provide and analyze all required matrix spike duplicates**.**

The following standard operating procedures (SOPs) are for collection of surface-water samples to be analyzed for inorganic constituents:

SOP 1—Preparation of sampling equipment for composite sample collection:

1. Put on gloves;
2. Remove sampler, bottle, and nozzle from plastic bags and assemble;
3. Dip sampler in lake, fill with native lake water, and empty through nozzle;
4. Collect aliquot of native lake water with the sampler and pour into churn splitter through the funnel; repeat until the churn splitter contains 2 to 4 liters of native lake water;
5. Remove churn splitter and inner plastic bag from carrier and outer plastic bag (outer bag remains in carrier);
6. Thoroughly circulate water in churn splitter with churn paddle;
7. Force spigot through the remaining plastic bag (inner bag) and drain water through spigot; and
8. Pull bag over spigot, rotate churn splitter so that spigot is away from hole in bag, and place churn splitter and inner bag into outer bag and carrier.

SOP 2—Sample collection using the DH95 sampler

1. Establish 2 cross sections perpendicular to lake width and length;
2. Establish equal-width measuring points along the cross section so there are 15 measuring points;
3. Prepare sampler and churn splitter as described in SOP 1;
4. At the first sampling point, with nozzle of the sampler pointing directly away from boat, slowly lower the sampler from the surface of the lake to the length of the sampling pole and raise sampler back to the surface. Lowering and raising speed must be uniform;
5. Determine how full the sample bottle is after the first cross section. If the bottle is more than about $^{1/3}$ full, deposit the sample into the churn splitter. If the sample bottle becomes more than about ¾ full at any time during sampling, the sample must be discarded and recollected at the affected sampling points; and
6. Repeat steps 4 and 5 at each sampling point.

SOP 3—Sample collection using the DH95 Sample bottle without churn

1. Prepare sample bottle and sampler as described in SOP 1;
2. Sample reagent grade water and collect field blank;
3. Then dip the sample bottle in lake and collect sample for methyl mercury analysis.

SOP 4—Transfer filtered sample from churn splitter to laboratory sample bottles

1. Rinse outside of pump inlet tube with de-ionized water and gently shake to remove the majority of the rinsate;
2. Install peristaltic pump inlet tube into the churn splitter pail through capable funnel in lid to a depth below the surface of the sample;
3. Turn on peristaltic pump and pump approximately one liter of sample without collecting;
4. Install disposable filter capsule on end of outlet tube and pump approximately one liter of sample without collecting;
5. Pump sample into prepared laboratory sample bottle;
6. Rinse bottle cap with filtered sample and install on bottle;
7. Repeat 5 and 6 until all required bottles are filled.

Containers, whether empty or filled, will be sealed and stored in a clean environment to prevent contamination. For inorganic samples, the containers will be rinsed with filtered sample water before collecting the samples and adding any preservatives. All sample bottles and preservatives will be sent to the USFWS by TERL no earlier than 2 weeks before sampling; this will insure the sample bottles and preservatives are fresh and have not passed their shelf life.

2.1.2 Fish sampling

Trout and catfish were the fish species selected for sampling as they are the primary species permitted to be fished on the selected lakes by the Navajo Nation Fish and Wildlife Department. Additionally, these fish species have been observed being taken as food items by the bald eagle by the Navajo Nation Natural Heritage Program biologists. Fish samples will be collected at the lakes identified and will be used to measure contaminant concentrations in fish tissue of mercury

and other trace elements. Fish sampling using an electrofishing boat will be attempted at each of the 15 water-sampling locations along the perpendicular cross-sections in each lake. If insufficient catfish (or bass) or trout are available at these locations, then additional locations, as directed by the biologists, will be sampled until 20 fish that are similarly sized (i.e., within 100 millimeters) are obtained. Fishing operation data (e.g., locations, gear, total catch, and shocking seconds of effort), biological data, and measurements on individual fish will be entered on the field notes. A USFWS biologist will be on board during all of the fishing operations to ensure proper handling of the samples. Fish will be collected by net and placed in a live well until sample preparation.

Sample preparation will include anesthetizing the fish, weighing and measuring, removal and compositing of the fillet portion as well as compositing that portion which remains ("the remaining portion"). An examination tray lined with aluminum foil will be used for the dissection for each fish. The maximum total length (mouth closed and caudal fin dorso-ventrally compressed) to nearest mm will be measured using a measuring board. The total weight (to the nearest 0.1 kg using the spring balance or other mass balance) of fish, fillet, and remaining portion will be measured and recorded. To reduce metal contamination, a ceramic knife will be used to remove the fillet. Five similarly-sized fish (± 100 mm) will be composited into 4 samples for analysis. Each trout or catfish will be uniquely identified by an individual identification number, while the composite sample will also be identified by a unique sample number. In total, 4 composite fillet samples for both methyl mercury and trace element analyses as well as 4 composite remaining portion samples for trace element analysis will be collected.

Immediately after they are processed, packaged, and labeled, all samples of trout and catfish will be placed on dry ice in a chest freezer and shipped to the analytical laboratory. All samples will be transported in an USFWS vehicle. Custody forms will be used for transfer of samples between authorized individuals, showing the dates(s) when delivered and received by the Laboratory.

We used the USEPA (2000) guidelines for determining sample sizes of fish from each lake considering variability and budget. While we will attempt to collect additional samples of fish, the minimum number of fish we will attempt to collect was determined using Table 6-1 in USEPA (2000). Our study design's use of 5 composite samples of 5 fish each from 4 lakes has the power of between 60 to 90 percent to determine a statistically significant difference between the screening value of 0.3 ug/g, and the geometric mean concentration of each lakes fish community, depending on the variability of mercury within each fish. To increase the power of the study design, we will attempt to collect additional fish for additional sample composites but will likely encounter logistic difficulties in obtaining and processing more the 20 fish per day along with other sample collection, processing, and shipment.

2.1.3 Site access

Field work will be performed on the Navajo Nation. Access to sampling sites is limited to project personnel escorted by a member of the Navajo Nation at all times.

2.2 Field Measurements

Field measurement of water temperature, air temperature, barometric pressure, specific conductance, pH, dissolved oxygen, turbidity, and secchi disk transparency may also be measured at each site wherever surface-water samples are collected. All field measurements and applicable information will be recorded on field logsheets as follows: surface-water measurements will be recorded on the USFWS – Lake Water and Fish Quality Field Notes (Appendix C). Field measurements will be made after collection and processing of the surface-water and fish samples. Additionally, a simple measurement of light penetration will be made with a secchi disk, which is lowered into the water to record the depth at which it appears to disappear to the observer.

2.3 Equipment decontamination

Equipment, which includes pump tubing, samplers, sampler bottles, caps, nozzles, churn splitters, funnels, bowls, trays, measuring boards, etc., will be decontaminated in the USFWS water-quality laboratory prior to a field activity. Decontamination of sampling equipment may also occur in the field to prevent cross contamination between sampling sites.

The following procedure applies to all surface-water collection and fish preparation equipment:

Required supplies:

- Deionized water (DIW)
- Trace-element-free hydrochloric acid (HCl)
- Liquid detergent free of phosphates
- Disposable, non-powdered vinyl gloves
- Four nonmetallic, clear or uncolored polypropylene or high-density polyethylene basins
- Various nonmetallic, uncolored brushes
- Sealable plastic bags of various sizes
- Wash bottles with clear or uncolored caps

Procedure for cleaning equipment prior to entering the field:

1. Clean all four basins using the same procedure that is used for cleaning equipment described below;
2. Fill basins as follows:
   Basin 1: Detergent solution dilute to 0.2 percent with tap water;
   Basin 2: DIW;
   Basin 3: HCl, diluted to 5 percent with DIW;
   Basin 4 DIW;
3. Disassemble all equipment, immerse all parts in detergent solution (Basin 1) for 30 minutes;
4. Put on vinyl gloves;
5. Scrub each piece of equipment with detergent solution; then transfer equipment to DIW (Basin 2);

6. Change gloves;
7. Rinse each piece of equipment with DIW until soap bubbles are no longer present; then place in HCl solution (Basin 3); soak for 30 minutes;
8. Change gloves;
9. Transfer each piece of equipment with DIW and place on clean plastic sheet;
10. Thoroughly rinse each piece of equipment with DIW and place on clean plastic sheet;
11. Conduct Step 10 two more times;
12. Place all equipment in appropriately-sized outer and inner plastic bags and seal.

To prevent cross-contamination between sites, the following procedures are conducted for all equipment that will be reused during a sampling event without undergoing procedures described above:

Procedure for field cleaning of pump tubing and sample processing chamber (pump tubing is to cleaned in the sample processing chamber):

1. Put on gloves;
2. Using pump, pass 1 liter HCl solution through pump tubing;
3. Using pump, pass 2 liters DIW through pump tubing;
4. Double bag pump tubing;
5. Remove and discard preservation chamber cover;
6. Swab surface on which the processing chamber sits with DIW.

Procedure for field cleaning of sampler and churn splitter:

1. Put on gloves;
2. Disassemble sampler and churn splitter;
3. Thoroughly rinse all parts with DIW;
4. Thoroughly rinse all parts with HCl solution;
5. Thoroughly rinse all parts with DIW;
6. Conduct Step 5 two more times;
7. Reassemble sampler and place in plastic bag; reassemble churn splitter and place in plastic bag;
8. Place single-bagged sampler and churn splitter in second plastic bag and place double-bagged equipment into churn-splitter carrier.

2.4 Environmental Sampling

Environmental-sample and associated blank-sample (QC) collection, preservation, custody, and handling will be conducted according to standard USFWS protocols. The quality of these activities will be monitored by reviewing the results of analysis of QC samples. Detailed descriptions of procedures to be used for assessing water-quality conditions by collecting, preserving, maintaining chain-of-custody procedures, and handling of environmental samples from surface water and fish will be provided in SOPs to follow first review.

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