

**CONTINUED MONITORING of WATER QUALITY STATUS**  
**and TRENDS in COEUR d'ALENE LAKE, IDAHO**

**With implications to long-term lake management and assessing lake response**  
**to environmental clean-up efforts in the Coeur d'Alene - Spokane River Basin**

**QUALITY ASSURANCE PROJECT PLAN**  
**ADDENDUM 2012**

**for field sampling by the Coeur d'Alene Tribe and Idaho Dept. of Environmental Quality**  
**and chlorophyll and trace-metals laboratory analyses by the U.S. Environmental**  
**Protection Agency Region 10 Manchester Environmental Laboratory**

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**January 2012**



## PART A. PROJECT MANAGEMENT

### A1 TITLE AND APPROVAL

Quality Assurance Project Plan for the Coeur d'Alene Lake Monitoring Program  
Coeur d'Alene, Idaho

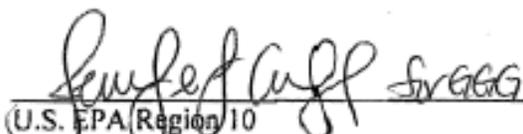
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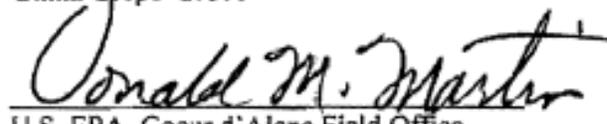
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## ABBREVIATIONS AND ACRONYMS

As	arsenic
BEMP	Basin Environmental Monitoring Plan
BEIPC	Basin Environmental Improvement Project Commission
CaCO <sub>3</sub>	calcium carbonate
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
Cd	cadmium
CDX	Central Data Exchange
chl <i>a</i>	chlorophyll <i>a</i>
CLP	contract laboratory program
COC	chain of custody
DQI	data quality indicators
DQO	data quality objectives
Fe	iron
GPS	global position system
IDEQ	Idaho Department of Environmental Quality
LMP	Coeur d'Alene Lake Management Plan
Mn	manganese
MS/MSD	matrix spike/matrix spike duplicate
N	nitrogen
P	phosphorus
PAR	photosynthetically active radiation (400-700 nm)
Pb	lead
PM	project/program manager
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RPD	relative percent difference
SOP	standard operating procedure
SRM	standard reference material
STORET	STOrage and RETrieval database, USEPA
TLG	Technical Leadership Group of the BEIPC
Tribe	Coeur d'Alene Tribe
TWRI	Techniques of Water-Resource Investigations
µm	micrometers
µg/L	micrograms/liter
USEPA	U.S. Environmental Protection Agency

USGS  
WQX  
Zn

U.S. Geological Survey  
Water Quality Exchange  
zinc

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## **A4 PROJECT / TASK ORGANIZATION**

The Coeur d'Alene Lake Monitoring Program began in the spring of 2007 and will be conducted by the Coeur d'Alene Tribe within tribal reservation waters and the Idaho Department of Environmental Quality (IDEQ) within State jurisdictional waters. The Tribe and IDEQ seek the funding necessary to ensure that this effort continues for the long-term.

This document is a quality assurance project plan (QAPP) for the field events, both collecting physical measurements and water samples, for the lake monitoring program. This QAPP has sufficient detail to also serve as a Work Plan for the monitoring program. This QAPP has been prepared in accordance with USEPA QA/G-4 and USEPA QA/R-5 requirements (USEPA 2000, 2001a). It is required because the Tribe and IDEQ are seeking USEPA assistance for laboratory analyses of the collected samples by the USEPA Region 10 laboratory at Manchester, Washington, or an approved contracted laboratory.

### **A4.1 IDEQ Program Manager**

Glen Rothrock of the Coeur d'Alene Regional Office (IDEQ program manager for the Coeur d'Alene Lake Management Plan), will be the program manager (PM). The IDEQ PM is responsible for the overall performance of IDEQ field operations, including adherence to this QAPP. Other responsibilities include:

- validation of data prior to entry into the EPA STORET system
- liaison with EPA laboratory representatives
- liaison with the Tribe PM to coordinate field activities and ensure that sampling techniques and methodologies as described in this QAPP are followed

Glen Pettit of the Coeur d'Alene Office will be the coordinator of IDEQ field sampling activities. Responsibilities include:

- maintenance and calibration of field measurement equipment
- pre-sampling trip cleaning of water sampling equipment
- ensuring that proper supplies are on hand including reagents that do not exceed stated shelf-life
- sample logging, chain-of-custody procedures, and sample shipping
- implementation of appropriate health and safety protocols during IDEQ field efforts

Becki Witherow of the Coeur d'Alene office will be the IDEQ limnologist for the LMP. Responsibilities include:

- data interpretation
- computer model analysis
- scientific report writing

Jake Watkins of the Coeur d'Alene office will be the IDEQ Water Resources Technician. Responsibilities include:

- data entry
- aiding in pre- and post-sampling efforts

Tom Herron, Supervisor, IDEQ Water Quality Protection Unit of the Coeur d'Alene field office, will be responsible for overall project management. This includes staff assignments, review and approval of equipment and supply expenditures, conduct and accountability of project staff, and assuring quality assurance on the project level.

#### **A4.2 Coeur d'Alene Tribe Program Manager**

Scott Fields, of the Coeur d'Alene Tribe's Lake Management Department will serve as Program Manager for the Tribe's involvement in this effort, with responsibilities equivalent to those described above for the IDEQ PM. Michael George Jr., Water Resources Technician under the supervision of Dale Chess (Tribal Water Resources Limnologist), will serve in a similar capacity as described above for the IDEQ field coordinator. Dr. Chess will also be involved to some extent in all aspects of this effort by the Tribe, including Program Management.

#### **A4.3 USEPA QA Officer/Regional Sample Control Center (RSCC) Coordinator**

The USEPA QAO will be responsible for reviewing and approving this QA Project Plan. The QAO may provide technical input on proposed sampling design, analytical methodologies, and data review. The RSCC will also coordinate EPA Regional laboratory services.

#### **A4.4 Analytical Laboratories**

Analysis of water samples for trace metals, minerals (hardness, calcium, magnesium), and chlorophyll *a*, collected during the Coeur d'Alene Lake Monitoring Program, will be provided by the USEPA Region 10 Manchester Environmental Laboratory, or another contracted laboratory. The Cd'A Tribe has contracted Tshimakain Creek Laboratory (TCL), formally Spokane Tribal Laboratory, for nutrient analysis (nitrogen and phosphorus series). IDEQ has contracted TCL for dissolved ammonia and nitrate analysis and SVL Analytical for total nitrogen and the phosphorus constituent series. Nutrient samples at this time will be financed by IDEQ and the Tribe. Phytoplankton and zooplankton identification and enumeration will also be the responsibility of IDEQ and the Tribe. IDEQ and the Tribe have contracted with TG EcoLogic (an LLC arm of TerraGraphics) for phytoplankton ID and enumeration. These biological samples will be processed according to established methods and quality assurance procedures.

The USEPA laboratory is responsible for assuring that all analyses performed by their facility meet study and data quality objectives. These are outlined in (1) this QAPP or associated analytical methods, (2) the laboratory SOP, or (3) the facilities' internal quality assurance procedures. Contact information for the Manchester Laboratory is:

Gerald Dodo, Chemistry Supervisor  
Manchester Environmental Laboratory  
7411 Beach Drive  
Port Orchard, WA 98366  
360-871-8748

The Tshimakain Creek Laboratory and SVL Analytical are responsible for assuring that all nutrient analyses performed by their facility meet study and data quality objectives. These are outlined in (1) this QAPP or associated analytical methods, (2) the laboratory SOP, or (3) the facilities' internal QAP.

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## **A5 PROBLEM IDENTIFICATION / BACKGROUND**

The primary environmental concern in Coeur d'Alene Lake is the potential for mobilization of contaminants such as arsenic, cadmium, lead and zinc present in its bed sediments if lake bottom waters become depleted in dissolved oxygen as a consequence of eutrophication. These contaminants were introduced by historic mining and ore-processing activities upstream in the South Fork Coeur d'Alene River valley mining district (in which the 21 square mile Bunker Hill Metallurgical Complex Superfund site surrounding Kellogg, Idaho is located). Subsequently, all other areas where hazardous substances have come to be located (including the South Fork Coeur d'Alene River valley and major tributaries, the entire Coeur d'Alene River and adjacent floodplain downstream of its confluence with the South Fork, Coeur d'Alene Lake, and the upper Spokane River extending into Washington state) has been designated as an extension of the Bunker Hill Superfund site. In addition, this area is the subject of one of the largest and most complex Natural Resources Damage Assessment and Restoration (NRDAR) litigation and restoration actions in the Nation.

Previous studies in the early 1990s by USGS researchers (in cooperation with the State of Idaho, the Coeur d'Alene Tribe, and with funding from EPA) show that approximately 85% of the lake bottom area (the lake surface area is 129 square kilometers) is covered by sediments highly enriched in mining-associated metals contaminants ranging in depth from a few centimeters to well over a meter (Horowitz *et al.* 1993 and Woods and Beckwith 1997). Median concentrations of total cadmium, lead and zinc were 56, 1800, and 3500 milligrams per kilogram, respectively, while unenriched sediments from the lateral lakes along the St. Joe River near its mouth contained 2.8, 24 and 110 milligrams per kilogram, respectively. Most of these contaminants in surface and subsurface sediments are primarily associated with ferric oxides, not the original

sulfide ore minerals. Therefore, if lake bottom waters become depleted in dissolved oxygen as a result of decomposition of excess organic matter produced by increased nutrient loading to the lake (e.g. eutrophication), the ferric oxide complexes are likely to be readily soluble and the metals contaminants released into the overlying water column. These studies also indicated that Coeur d'Alene Lake at that time had a relatively large capacity to assimilate nutrients before exhibiting the adverse effects of eutrophication such as hypolimnetic anoxia. In addition, these studies indicated significant suppression of algal productivity by the elevated concentrations of dissolved zinc in lake waters.

Information from these studies was incorporated into a 1996 Coeur d'Alene Lake Management Plan (LMP) that was developed by an array of government, business, and citizen group entities (Clean Lakes Coordinating Council *et al.*, 1996). The 1996 LMP was based on voluntary actions, was never funded, and therefore, not effectively implemented.

Additional studies were funded by EPA and conducted by USGS researchers in 1999 to further define limnological conditions, to assess the fate and transport of mining-associated contaminants entering the lake, and to characterize contaminant release from lake bed sediments. Information from these studies was used by EPA in its Record of Decision (USEPA, 2002) for an interim remedy for the Bunker Hill Superfund Site Operational Unit 3 (e.g. those areas where hazardous substances have come to be located outside of the original 21 square mile ore-processing complex surrounding Kellogg and Pinehurst, Idaho). Although Coeur d'Alene Lake lies within this area, no remedy was selected. Instead, hazardous substances in lake waters and bed sediments are to be managed in-place (by maintaining a lake environment that does not lead to anoxic conditions in lake bottom waters and subsequent contaminant release from lake bed sediments) by means of a Lake Management Plan (LMP) jointly developed and implemented by the State of Idaho and the Tribe, using other regulatory and resource management authorities outside of the formal Superfund process.

As part of the Bunker Hill Superfund site remediation process, EPA continues to fund USGS to monitor hydrologic, sediment, mining-associated contaminants, and nutrients transport near the mouths of the lake's two primary inflows, the Coeur d'Alene and St. Joe Rivers, and the lake's outlet, the Spokane River. This effort is part of the Coeur d'Alene Basin Environmental Monitoring Plan (BEMP, USEPA 2003), begun in October 2003 to evaluate the long-term effects of cleanup actions.

Additional cooperative lake studies by the Tribe and USGS were conducted in water years 2004-2006. These studies were funded by an EPA Clean Water Act 104(b)(3) grant through the Coeur d'Alene Basin Environmental Improvement Project Commission (BEIPC) with the objectives of:

- 1) assessing current lake water quality conditions and trends with respect to potential mobilization of mining-associated metal contaminants from lakebed sediments,
- 2) identifying potential changes in those conditions compared to those reported by lake studies completed in the early 1990s, and
- 3) characterizing potential effects of ongoing environmental remediation efforts upstream.

A scientific report of the USGS studies was published in 2008 (Wood and Beckwith, 2008). Although there are significant methodological differences among the studies, results of this most recent study effort suggest that the lake is becoming more productive (as indicated by increased median euphotic zone chlorophyll *a* concentrations) than it was in the early 1990s.

In a related effort (and also supported by Clean Water Act 104(b)(3) funds through the BEIPC), researchers from USGS and the Centre for Water Research – University of Western Australia applied the 3-dimensional hydrodynamic **Estuary Lake COMputer** model (ELCOM). The capabilities to simulate the benthic flux of metals contaminants to / from lakebed sediments and the interactive effects of dissolved zinc on algal productivity were developed, and ELCOM was coupled to a **Comprehensive Aquatic Ecosystem DYNAMics** lake response / trophic status model (CAEDYM) for Coeur d'Alene Lake using newly-collected lake current and other physical data and historic data from the previous studies.

The validation simulation of the ELCOM-CAEDYM model was conducted for the year of 2004, since this year had the largest amount of data available. The simulation included four phytoplankton groups (cyanophytes, chlorophytes, cryptophytes, and diatoms). In addition to the phytoplankton, the simulation included organic matter state variables, nutrients and most inorganic ions of relevance. The model simulations compared well with available field data. In particular, the chlorophyll *a* and Zn concentrations were successfully reproduced, both in terms of spatial and temporal variability. Other variables of interest such as carbon, nutrients and the major geochemical elements were also reasonably reproduced. In general, the model successfully captures the dynamics of primary importance within the system such as inflow loading, sediment-water interactions, primary production and organic matter cycling within the water column. The physical, chemical and biological data gathered under this QAPP will provide the annual baseline for simulations and model refinement. A framework is being produced to guide the input for model simulations of various scenarios unique to the Coeur d'Alene Lake ecosystem (e.g., increased loading and reduced zinc). The Coeur d'Alene Lake ELCOM-CAEDYM model represents a significant advance to the current state-of-the-art in 3D ecological modeling.

Initial ELCOM-CAEDYM modeling results indicate:

- 1) the Zn bound within algal biomass is a small component of the total Zn mass but the cycling of Zn through the algae acts as a large Zn flux mechanism
- 2) deposition of particulate forms of Zn (mainly Zn in the form of diatom biomass and a detrital component) is roughly equivalent to the amount of dissolved Zn released from the sediment to the water column
- 3) epilimnetic median zinc concentrations appear to have declined since the early 1990s, but are expected to remain high enough to suppress phytoplankton productivity well into the foreseeable future
- 4) lake response to changes in Zn and nutrient loadings will be relatively modest due to the extreme sensitivity of the phytoplankton to Zn (particularly *Chlorella*)

- 5) reduction of Zn loading in inflow waters would have to be reduced by one to two orders of magnitude before suppressive effects will begin to disappear
- 6) remediation in the mining-affected watershed is unlikely to result in a noticeable eutrophication response within the main lake, assuming nutrient inputs do not increase
- 7) phosphorus limitation is currently keeping biomass low, and eutrophication pressures need to be managed to prevent increased algal biomass

Results from the USGS scientific studies report for the 2004-2006 lake monitoring, and results from the ELCOM/CAEDYM modeling project (Hipsey *et al.* 2007) indicate that a combination of low phosphorus and Zn toxicity currently is keeping the lake's algal biomass at an acceptable level. Efforts to alleviate loadings of Zn from the Coeur d'Alene River are unlikely to produce a significant reduction in Zn toxicity in the near term, primarily due to the continued loading from the watershed (although apparently reduced) and from the lakebed sediment. However, decision-makers should pay careful attention to continued eutrophication pressures because the lake may respond significantly to increased phosphorus input – with or without Zn toxicity. The south end of the lake is already showing signs of this; if the P loading is not effectively managed the potential exists for the symptoms of eutrophication to promulgate further downstream (e.g. into the deeper, main body of the lake). The model simulations suggest that increased phosphorus loading will either produce increased diatom biomass (if the Zn toxicity remains relatively constant), or result in increased biomass of a mixed assemblage of phytoplankton species, including more greens and blue-greens (if Zn concentrations in the lake decrease considerably). Since the diatoms are mildly photo-inhibited and tend to form a deep chlorophyll maximum, an increase in diatom biomass rather than greens and/or blue-greens will potentially result in fewer nuisance side-effects. However, the overall biomass within the lake should remain below 3 µg chl *a*/L if P loading is appropriately managed.

The Coeur d'Alene Lake Monitoring Program will continue in spring 2012, or earlier, to sample a large rain-on-snow event. It will be conducted by the Coeur d'Alene Tribe within tribal reservation waters and by the IDEQ within State jurisdictional waters. The overall objectives of this effort are:

- 1) to continue monitoring limnological conditions and trends and their potential effect on remobilization of contaminants (such as arsenic, cadmium, lead and zinc) and nutrients (nitrogen and phosphorus) from lake bed sediments;
- 2) to continue collecting physical and chemical data relevant to the predictive capabilities of the ELCOM-CAEDYM model;
- 3) the State and Tribe intend to develop the capability to use the ELCOM-CAEDYM model locally to utilize the continued lake water quality monitoring information in the decision-making process for managing lake water quality and historic mining-associated hazardous substances that are present in lake waters and bed sediments, and throughout the lake's catchment basin;

- 4) to serve as the basis for development and implementation of a joint State – Tribe Lake Management Plan (which will ultimately also involve other governmental entities and public and private interest groups) and to assess the effectiveness of such efforts over time.

## **A6 PROJECT / TASK DESCRIPTION**

Details of the lake monitoring program are presented in Section B. In this Section (A6), a general description is given of the work to be performed, where it will take place, and what conditions will be measured.

Lake monitoring will be conducted at a total of ten (11) sites: 1) four sites will be sampled by IDEQ in the deep northern portion of the lake under State of Idaho jurisdiction, along with four shallow bay stations, 2) three sites will be sampled by the Tribe in waters within the Reservation boundary: in the shallow southern portion of the main body of Coeur d'Alene Lake, a site within the lower St. Joe River, and Chatcolet Lake (lateral to the St. Joe River). Ten of these sites are sampling stations established and monitored by the USGS and the Tribe in 1991-92, and again in 2003 – 2006 (Figure B-1 and Table B-1, sites C1, C2, C3, C4, Windy Bay, Loffs Bay, Carlin Bay, Cougar Bay, C5, and C6). A site was established by the Tribe in the lower St. Joe River to better characterize eutrophication-related effects and constituent transport. The above sampling sites were selected to depict lake conditions from southern shallow waters influenced by inflow of the St. Joe River and southern tributaries, mid-lake conditions as influenced by inflows from both the St. Joe and Coeur d'Alene Rivers, deep northern pool waters, and northern pool shallow bays as influenced by northern tributaries.

Each year there will be 7 to 8 sampling visits to each site. The schedule of sampling visits (Table B-2) is designed to capture various lake conditions from high inflow in late winter or spring, summer stratification, and through fall turn-over. On each visit physical properties will be measured, including water clarity and photosynthetically active radiation (PAR) in the euphotic zone, and profiles through the water column of water temperature, dissolved oxygen (DO), % DO saturation, pH, specific conductance, turbidity, and chlorophyll *a* fluorescence.

Lake samples for analysis of chemical constituents will be taken in multiple zones in the water column at each sampling site (Table B-3), generally following the sampling scheme utilized in the Tribe and USGS studies in 1990-94 and again in water years 2004-2006. These zones are:

- 1) Composite sample of the euphotic zone (the sunlit zone where photosynthesis occurs, the lower boundary is defined as the depth at which 1 % of ambient solar radiation is received).
- 2) Depth at which maximum chlorophyll *a* fluorescence occurs. In the 2004-2006 Tribe/USGS studies, researchers using more sophisticated water column profiling instrumentation than that used in the 1990-94 studies observed a pronounced but relatively narrow zone of increased chlorophyll *a* concentration in the vicinity of the thermocline, particularly in late summer during the peak of the growing season and thermal stratification. This observation suggests that traditional euphotic zone composite sampling methods used in previous studies did not adequately represent

conditions of biological productivity throughout the euphotic zone and may have resulted in an underestimation of chlorophyll *a* concentrations. Approximately mid-way through the 2004-2006 studies, USGS researchers began collecting discrete samples at the depth of maximum chlorophyll fluorescence. IDEQ and the Tribe intend to continue such sampling, which over time, may provide a more accurate indication of actual primary productivity in Coeur d'Alene Lake.

- 3) Discrete samples at approximately 10 m intervals throughout the hypolimnion (the zone below the thermocline) at deep northern pool stations. Previous studies indicate a trend of increasing zinc concentrations with depth, especially during the late summer. Two potential mechanisms for this trend have been hypothesized: benthic flux of zinc from lake bed sediments; or zinc being stripped from the euphotic zone by algal biomass and organic detritus and deposited at depth as it sinks through the water column. It is hoped that discrete samples collected throughout the hypolimnion can resolve these potential mechanisms, and minimize the potential for erroneously concluding that epilimnetic zinc concentrations are declining as result of upstream remediation, when indeed such declines may be more the result of increased algal productivity in the euphotic zone and the resulting bottom-ward flux of zinc associated with organic detritus.
- 4) A discrete sample is taken 1 meter above lakebed sediments. This sample is intended to reflect near-bottom conditions as influenced by benthic flux of contaminants and nutrients out of lakebed sediments, perhaps in response to eutrophication-induced seasonal dissolved oxygen deficits. It must be collected carefully so as not to entrain bottom sediments.

Chemical constituents for laboratory analysis are detailed in **Table B-4**, including constituent sets within each of the four or five sampling zones. These parameters (particularly nitrogen, phosphorus and chlorophyll *a*) will be used for assessing the status and trends in lake trophic conditions. Trace metals (arsenic, cadmium, lead and zinc) are toxic to aquatic life; maximum allowable concentration criteria are specified by both State of Idaho and Tribal water quality standards (Table A-1 for Idaho standards, full promulgation of Tribal standards are pending but are equivalent to those of the State of Idaho). These concentration criteria vary with hardness; hence, hardness (including actual concentrations of calcium and magnesium) also will be determined.

**Table A-1. Numeric Criteria of Metals Concentrations Sampled in the Coeur d'Alene Lake Monitoring Program - Idaho Water Quality Standards (IDAPA 58.01.02.210, as revised 4-11-06).**

Compound	Aquatic life		Human health for consumption of	
	<sup>a</sup> CMC µg/L	<sup>b</sup> CCC µg/L	Water & Organisms µg/L	Organisms Only µg/L
Arsenic	340 c	150 c	50 d	50 d
Cadmium	0.42 e	0.25 e,g	f	f
Lead	14 e	0.54 e	f	f
Zinc	36 e	36 e	7400	26000

For metals listed above, aquatic life criteria are expressed as dissolved metal concentrations.

- a. Criterion Maximum Concentration
- b. Criterion Continuous Concentration
- c. Arsenic criteria expressed as a function of the water effect ratio (WER).
- d. Inorganic form only.
- e. Cadmium, lead, and zinc calculated with a hardness of 25 mg/L CaCO<sub>3</sub>.
- f. No numeric human health criteria have been established for these contaminants.
- g. Cadmium CCC may be calculated down to a hardness of 10 mg/L CaCO<sub>3</sub> (IDAPA 58.01.02.210.03.c.i, as revised 3-29-10)

The apparent trend of declining zinc concentrations within the upper waters of the lake is of particular concern because it may indicate the effectiveness of clean-up efforts within Superfund areas upstream. However, this apparent decrease in epilimnetic zinc concentrations (especially if combined with corresponding increases in hypolimnetic zinc concentrations in late summer) may simply be an indication that zinc is removed from the epilimnion in algal biomass and organic detritus and deposited in the hypolimnion. Alternatively, apparent declines in epilimnetic zinc concentrations may also be an indication (especially if accompanied by measurable increases in chlorophyll *a* concentration or shifts in the phytoplankton community species composition) that algal productivity is responding to increased nutrient availability. Considerable care and limnological expertise will be needed in identifying and interpreting the existence and potential causes of such apparent trends.

The constituent set also includes iron and manganese. Fe and Mn hydroxides can sequester phosphorus compounds, and act as flocculants to adsorb trace metals.

## **A7 DATA QUALITY OBJECTIVES FOR MEASUREMENT DATA**

The overall objectives for an annual, long-term Coeur d'Alene Lake Monitoring Program are presented in Section B1, along with the rationale and specifics of the sampling design to meet those objectives (Sections B1 – B4). The selection of lake sampling sites, water column physical measurements, chemical constituents for analysis, and water column sampling zones, follows closely the sampling design used by the USGS and Tribe beginning in 1991 through the most current monitoring effort of 2003 – 2006. The objectives through time have remained similar: to

provide a link and feedback between limnological conditions defined through monitoring and research, and lake management decisions regarding land use practices which prevent eutrophication trends that could lead to increased mobilization of metal contaminants from the lake bed sediments. A tool that will be added to the link between lake data and lake management decisions is development of the ELCOM-CAEDYM model (see discussion in Section A5).

The data quality objectives (DQOs) of the lake monitoring program are to provide sufficient limnological data of sufficient quality to accurately characterize water quality status and trends within the lake to support technically sound and socioeconomically feasible lake water quality management programs and actions. Of equal importance to sample design, is that lake management decisions are not made based on inaccurate data due to experimental error (e.g. contamination of samples, faulty equipment, improper calibration, poor accuracy of analysis, and poor duplication of analysis) and even inaccurate transcription and recording of data. For analysis of chemical constituents and physical parameters through instrumentation, there are the data quality indicators (DQIs): precision, accuracy, bias, completeness, representativeness, comparability and sensitivity. These terms are defined in Section B5.2. The methods that IDEQ, the Tribe, and the contracted laboratory, will use for determining DQIs are described in detail in Sections B5 through B10.

## **A8 TRAINING REQUIREMENTS / CERTIFICATION**

Field measurements, lake water sample collection, and sample submittal to contracted laboratories will be conducted by Tribe and IDEQ staff experienced in limnological sampling and data management, including the calibration and use of specific monitoring instrumentation and sampling equipment. The State and Tribe field crews will follow their respective Standard Operating Plans (SOPS) and this QAPP for conducting all field activities. Health and safety issues during field activities are the responsibility of the field crews and responsible governments conducting the field effort.

## **A9 DOCUMENTATION AND RECORDS**

Documentation required for this monitoring effort will include: this QAPP, instrument calibration logbooks, field logbooks, water column profile field data sheets, laboratory data reports, computer data files, and subsequent data evaluation reports and presentations. Given the expected long-term nature of this lake monitoring program, the data generated will be compiled and archived in a standardized format using electronic spreadsheet and database software as well as hard copy files. In addition, it is important that the collected data be interpreted into relevant information that are then incorporated into the resource management decision process. The routine release of data reports and convenient access to available data will allow interested stakeholders to review and assess the data in support of lake water quality management decision processes. The lake monitoring data will be made available by several mechanisms:

- EPA STORET through the CDX web-based data management system
- Annual data summary reports
- Five-year data analysis and assessment reports

- Internal Tribe and IDEQ Excel spreadsheets for collected physical data and water chemistry data that can be made available upon request

### **A9.1 Field Documentation**

Field documentation in a logbook is mandatory for field measurements and sample collection. A designated field member will document all field activities in a field logbook that is weatherproof, bound, and paginated. Each page of the logbook will be dated and signed by the note-taker. All entries in the logbook will be made with waterproof ink. Any entry errors made during documentation will be crossed out with a single line followed by the note-takers initials. The corrected information will be initialed and dated.

For pre-trip calibration procedures of field measurement equipment (at the agencies office lab), a logbook will be maintained of calibration information and results.

There will be field forms for manual entry of the water column profiles for light measurements taken with the Li-Cor<sup>®</sup> system and for water column profiles taken with the Hydrolab<sup>®</sup> DS5 multiprobe (Appendix A). While the Hydrolab<sup>®</sup> multiprobe will be connected to an on-board lap-top computer, receiving and storing profile data electronically through Hydras 3 LT software, experience has shown that problems can occur with this on-board electronic storage capability, and thus a backup field form of manually entered profile data is important.

As water samples are prepared for shipment to the laboratory, there will be laboratory submittal forms and chain-of-custody forms filled out by IDEQ and Tribe staff. Copies of these forms will be made for IDEQ and Tribe records.

All logbooks, field forms, and laboratory submittal forms will be systematically filed and retained long-term at the IDEQ and Tribal offices.

### **A9.2 Laboratory Documentation**

Laboratory documentation requirements are delineated in the laboratory contracts and include specifications of data report composition, report format, turnaround time, and records retention. Laboratory data are recorded in a CLP format or similar format, including sample identification, analysis data, parameter values, and detection limits.

### **A9.3 IDEQ and Tribe Documentation**

Hard copy field data and laboratory results will be entered into Excel spreadsheet files following the QA procedures in Section B10. Data logger and other electronic data, downloaded and processed, or as received from the laboratory, will be compiled into standard Excel formatted files. IDEQ and the Tribe will each be responsible for electronic data entry from their respective sampling stations. However, IDEQ and the Tribe will develop a joint format for the various Excel spreadsheets to be maintained on respective office computers.

#### **A9.4 EPA Central Data Exchange (CDX) web-based data management system**

In 2009, EPA adopted a web-based data management system for data submission to, and exchange of data from, the national STORET repository database. This system is the Central Data Exchange (CDX). For data submission, CDX uses a web-based framework called Water Quality Exchange (WQX). The Tribe and IDEQ currently have active CDX accounts for submitting Coeur d'Alene Lake data to STORET using WQX and will continue to do so.

## **PART B. MEASUREMENT / DATA ACQUISITION**

### **B1 SAMPLING PROCESS DESIGN**

The monitoring program described in this QAPP was designed to provide sufficient temporal and spatial data to characterize water quality status and trends of Coeur d'Alene Lake over time. The overall objectives of this effort are:

- 1) to continue monitoring limnological conditions and trends and their potential effect on remobilization of contaminants (such as arsenic, cadmium, lead and zinc) and nutrients (nitrogen and phosphorus) from lake bed sediments;
- 2) to continue collecting physical and chemical data relevant to the ELCOM-CAEDYM model;
- 3) to utilize the resulting information in the decision-making process for managing lake water quality and historic mining-associated hazardous substances that are present in lake waters, bed sediments, and throughout the lake's catchment basin;
- 4) to serve as the basis for development and implementation of a joint State – Tribe Lake Management Plan.

#### **B1.1 Sampling Sites, Sampling Frequency, and Parameters Sampled**

##### Sampling Locations

Lake water column measurements and samples will be collected at eleven sites (Figure B-1). IDEQ will sample at eight sites north of the Tribal reservation boundary (north of Harrison). These sites were established by USGS and sampled in 1990-94, and again in 2004-2006. These are USGS sites C1 (southeast of Tubbs Hill), C2 (Wolf Lodge Bay), C3 (southwest of Driftwood Point), C4 (northeast of University point), Windy Bay, Loffs Bay, Carlin Bay and Cougar Bay.

The Tribe will sample at two southern Lake sites established by USGS: site C5 located mid-lake between Brown's Point (but erroneously called Blue Point by USGS in the 1990-94 studies from out-dated maps) and Chippy Point, and USGS site C6 located in Chatcolet Lake (over the deepest area northwest of Rocky Point). The Tribe established a new station, SJ1 in the lower St. Joe River in the deep hole upstream of the USGS gage 12415140, St. Joe River near Chatcolet ID. Weak stratification and significant near-bottom dissolved oxygen deficits have been observed by Tribal staff at this site in the past, particularly in late summer. It may reflect conditions of nutrient enrichment and increased biological productivity in lower St. Joe River, where very little water quality monitoring has been conducted in the past.

##### Sampling Frequency and Timing

Sampling will be conducted seven to eight times annually (Table B-2). The timing of sampling visits coincides with specific lake conditions of interest throughout the year as shown in

Table B-2. The Tribe and IDEQ will coordinate their respective field sampling events so that they both are conducted during the same week.

### Physical Measurements Taken

Methods and equipment used for collecting physical measurements are detailed in Section B2. At each sampling site, IDEQ and the Tribe will record GPS location and station water depth. Water column profiles will be taken of Photosynthetically Active Radiation (PAR), water temperature, dissolved oxygen, %DO saturation, pH, specific conductance, chlorophyll *a* fluorescence, and turbidity. A Secchi disc transparency depth measurement also will be taken from the shady side of the boat both with and without the use of a view tube.

### Water Samples for Chemical Constituents

Methods and equipment used for water sampling are detailed in Section B2. Four water column zones will be sampled at the pelagic sites, and one composite sample will be collected from each of the bay stations unless bay station depth is greater than 1% PAR. In this event, a sample 1 meter off the bottom will be collected. Table B-3 lists the analytes sampled in each zone at each sampling station, along with the total annual number of analyte samples (**Table B-4**).

- 1. Euphotic Zone Composite:** five equally spaced samples from 1.0 m below the surface to the depth where underwater Photosynthetically Active Radiation is 1% of the surface value. Euphotic zone composites will be collected on each visit at all sampling locations. Subsamples will be analyzed for total and dissolved nutrients, total and dissolved metals, minerals (hardness, dissolved calcium, and magnesium), and chlorophyll *a*. (See Appendix B for Tribe's SOP for a detailed description of euphotic zone sampling, churn-splitter compositing and subsampling, and sample handling and processing procedures used in the 2004-06 Tribe / USGS Lake studies; essentially the same procedures will be used by Tribal field crews in this effort).

During rain-on-snow events, flood events, and spring high flow when lake water can be highly turbid, IDEQ and the Tribe will selectively post-filter the dissolved metals from the 0.45  $\mu\text{m}$  capsule filter. The Tribe will post-filter through a 0.2  $\mu\text{m}$  membrane filter, and IDEQ will filter through a 0.1  $\mu\text{m}$  Stericup® filter. These will be additional dissolved metals samples. In 2007 – 2009, both the IDEQ and Tribe experienced fine colloidal materials passing through the 0.45  $\mu\text{m}$  capsule filters and presenting a visual appearance of particulates floating within the filtered samples. We are interested in determining whether the 0.20 and 0.10  $\mu\text{m}$  filters eliminate interference from fine colloids.

Subsamples will also be collected for phytoplankton and zooplankton identification and enumeration by a separate contractor to be supported by IDEQ and the Tribe. Initially, a 125 mL subsample for phytoplankton will be withdrawn from the churn splitter containing the euphotic zone composite and preserved with Lugol's iodine for subsequent identification and enumeration of taxa present by the settling chamber and inverted microscope technique.

2. **Zone of Maximum Chlorophyll *a*:** a discrete sample collected at the depth of maximum chlorophyll *a* fluorescence. USGS began sampling at the chlorophyll *a* maxima depth in 2005 at all sampling sites in late summer (June, July, and August). Therefore, sampling and analysis at the depth of maximum chlorophyll *a* fluorescence likely will occur on only three or four of the sampling visits, and probably only at the deep-water sites in the main body of the Lake (C1, C2, C3, C4, and C5). Analysis parameters will include total and dissolved nutrients, total and dissolved metals and minerals, chlorophyll *a*, and phytoplankton identification and enumeration.
3. **Discrete sampling at 20 m and 30 m:** in the northern pool stations, USGS sampled at these depths for the entire array of constituents (note: given the depth of site C3, these discrete samples will be collected at 25 and 40 m). The primary trend of interest to IDEQ is for zinc, where April – August concentrations increased with depth. In 2007, dissolved and total zinc was analyzed at sites C1 and C4 on each sampling visit at these depths in the hypolimnion. In 2008, IDEQ added total and dissolved nutrients and metals. As discussed earlier, there may be several explanations for the apparent trend in zinc decline since 1992, and care will need to be exercised in drawing conclusions that the decrease is attributable to the effectiveness of environmental remediation upstream, or due to increased stripping of zinc from the euphotic zone by phytoplankton biomass and organic detritus.
4. **1 meter above lake bottom:** a discrete sample with depth determined from the Hydrolab<sup>®</sup> profile (depth to bottom). Samples are taken at each station on each sampling visit. Samples will be analyzed for total and dissolved nutrients, total and dissolved metals, and minerals (hardness, dissolved calcium, and dissolved magnesium).

## **B2 SAMPLING METHODS**

This section describes the standard procedures to be used during sample collection, field data generation, and laboratory analysis of samples collected under the monitoring program described in Section B1 of this QAPP. The methods described in this section were selected to provide representative, reproducible data with respect to the status and trends in limnological conditions in Coeur d'Alene Lake and be as comparable as possible to previous data collected by the USGS and Tribe.

### **B2.1 Physical Parameters Measured by Instrumentation**

#### IDEQ Protocol

Refer to Section B6 for maintenance and calibration procedures of instruments that IDEQ will use in the lake monitoring program.

IDEQ will use a 21 foot Hewes Craft aluminum-hull boat for sampling seven sites within State jurisdictional waters. On each sampling visit, a GPS waypoint is used to locate the sampling sites. The exact latitude and longitude of the boat will be recorded in the field log book prior to sampling. At the end of the sample efforts a final GPS reading and distance from point will be

recorded in the field logbook. An initial station water depth will be recorded from an on-board sonar.

A Li-Cor<sup>®</sup> system of LI-1400 DataLogger, deck-side 190SA Quantum Sensor, and a 193SA Underwater Spherical Quantum Sensor, will be used to record a water column profile of PAR. The deck-side 190SA provides a reference sensor for light incident on the water's surface (400 to 700 nm waveband). The 193SA underwater sensor is secured to a lowering frame and lowered on sun exposed side of the boat down the water column at 1-3 meter intervals to record PAR from multiple directions. Readings from the 193SA divided by the 190SA, as calculated and displayed on the data logger output, provides percent PAR as referenced by surface light. Readings are taken at 0.25-3 m intervals down to the level where PAR is 1% of light intensity at the surface (for euphotic zone composite samples). Readings are manually recorded on field forms (Appendix A), as well as stored in the LI-1400 DataLogger and then exported into an Excel spreadsheet.

Secchi disc transparency depth measurements will be taken with a 20 cm black and white disc. The Secchi disc will be lowered in the water on the shaded side of the boat until it is no longer visible and the depth noted to approximately the 0.1 meter increment. Secchi disc readings shall be taken and recorded both with and without the aid of a view tube.

IDEQ will profile the water column with a Hydrolab<sup>®</sup> DS5 multiprobe instrumentation (with 100 m cable), connected to an on-board lap-top computer running Hydras 3 LT software. The lap-top computer is powered by a 12 volt power inverter connected to the boat's battery.

IDEQ Ambient air temperature will be collected from the newly installed IDEQ MET station located on the shore of Coeur d'Alene Lake at McDonald Point.

Before deployment, the multiprobe is calibrated to a depth of 0 meters. The initial profile reading is taken at 0.5 m depth. The following parameters are recorded: water temperature, dissolved oxygen and %DO saturation (LDO sensor), pH, specific conductance, chlorophyll *a* fluorescence (the Hydrolab<sup>®</sup> includes a Turner Designs chlorophyll *a* sensor), and turbidity. While the Hydras 3 LT software provides for electronic data storage in Excel spreadsheet files, profile readings will also be recorded manually on field forms. The multiprobe is then lowered through the water column and the readings recorded.

During isothermal conditions, or nearly so (late fall through spring visits), the water column profile readings are taken at 2 m intervals down to 20 meters (except for the interval from 17 – 20 m) and then at 5 m intervals to the lake bottom (with final readings at 1 m off bottom and approximately 0.2 m off the bottom). An accurate bottom depth can be obtained using the Hydrolab<sup>®</sup>. During periods of initial stratification and established stratification (May – October), profile data is obtained at 1 m intervals from surface – 20 m and then at 5 m intervals to the bottom. During stratification, the water column profile is examined for a maximum layer of chlorophyll *a* fluorescence for collection of a discrete sample at that depth.

#### Tribe Protocol

Tribal field sampling staff will generally follow accepted limnological procedures described by IDEQ above. A general Standard Operating Procedures (SOP) for field data and sample

collection by Tribal staff in this Coeur d'Alene Lake monitoring effort is presented in Appendix B (Procedures B1). It is essentially the procedures used in the 2004-2006 cooperative Tribe / USGS Coeur d'Alene Lake studies.

## **B2.2 Water Sample Collection, Tribe and IDEQ**

In general, the water sampling program will be conducted in accordance to the USGS standard procedures for sample collection, as described in the National Field Manual for the Collection of Water-Quality Data: U.S. Geological Survey TWRI, Book 9, chapters A1-A6. The TWRI manuals describe the procedures for:

- Selection of equipment and supplies for surface water sampling (Chapter A2, Lane *et al.* 2003)
- Preparation for water sampling (Chapter A1, Wilde 2005)
- Cleaning of equipment for water sampling (Chapter A3, Wilde 2004)
- Collection of lake water samples (Chapter A4, Wilde *et al.* 1999)
- Field processing of water samples (Chapter A5, Wilde *et al.* 2004)
- Handling and shipping of samples (Chapter A5)

The Tribe and IDEQ have established agreed upon sampling equipment and procedures for the water sampling program from the TWRI manual (Appendix B, Tribe SOP, Procedures B1). The exception is that IDEQ will perform a modified method for field filtration based on existing equipment and experience (Procedures B2). It will be the responsibility of the program managers to ensure that the procedures are followed and conducted in the same manner for both entities. Appendix B presents:

- Sampling equipment, supplies, and reagents
- Pre-visit procedures for cleaning sampling equipment in the respective office labs
- Procedures by field-crews in collecting lake samples and placing collected water in churn splitters, using clean-sampling procedures
- Filtration procedures for dissolved nutrients and metals, and chlorophyll *a*
- Procedures for transferring collected water to laboratory sample bottles
- Field procedures for sample preservation and holding
- Field cleaning procedures of sampling equipment between sample zone depths and between sampling sites

- Procedures for sample preservation and shipping to the laboratory
- Post-sampling trip equipment cleaning and instrument calibration check procedures

Table B-5 in this Section lists the recommended container sizes, container types, sample preservation, and holding times for each analysis, along with specified filters for dissolved constituents, specifications for acid preservation, and lab-certified constituent-free water for equipment and field blanks. Lake water samples collected for dissolved metals and nutrients will be field-filtered through 0.45 µm pore size capsule filters, and phytoplankton will be filter-entrained on 0.3 µm pore size Advantec glass fiber filters.

### **B2.3 Water Sample Analysis**

Lake water samples will be analyzed at the US EPA Manchester Environmental Laboratory in Washington, or at an alternative EPA contracted laboratory, using either EPA methods or procedures in Standard Methods for the Examination of Water and Wastewater, 21st Edition (American Public Health Association, 2000). Analytical methods for sample analysis are presented in **Table B-6**, along with target reporting limits and quality control criteria (precision, accuracy, and completeness). Lake water samples will be analyzed for:

- dissolved trace metals (cadmium, lead, zinc, and arsenic)
- total trace metals (cadmium, lead, zinc, and arsenic)
- total and dissolved iron and manganese
- total hardness, dissolved calcium, and dissolved magnesium
- chlorophyll *a*

Lake water samples for nutrients will be analyzed at the Tshimakain Creek Laboratory for Tribe samples and dissolved ammonia and dissolved nitrate for IDEQ, SVL Analytical analyze the phosphorus series for IDEQ samples, using either EPA methods or procedures in Standard Methods. Analytical methods for sample analysis are presented in **Table B-6**, along with target reporting limits and quality control criteria (precision, accuracy, and completeness). Lake water samples will be analyzed for the following nutrients:

- total nitrogen for IDEQ, total Kjeldahl nitrogen for Tribe (as N)
- dissolved ammonia (as N)
- dissolved nitrite (as N) (Tribe only)
- dissolved nitrate (as N)
- total phosphorus (as P)
- total dissolved phosphorus (as P)
- dissolved orthophosphate (as P)

Samples for phytoplankton and zooplankton identification and enumeration will be analyzed by standard accepted limnological practices.

### **B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS**

This section describes the procedures to be used for handling of samples in the field and to ensure that samples are packaged, shipped, and maintained under the proper chain of custody. USGS procedures for sample handling and shipping are detailed in TWRI Chapter A5, Section 5.5 (USGS 2002).

#### **B3.1 Sample Containers, Preservation, and Holding Times**

Sample containers, preservation requirements, and holding times are listed in Table B-5.

#### **B3.2 Sample Labeling**

In the field, sample containers will be labeled with an indelible marker. Label information includes the site identification, the date and time of sampling, type of analysis and the preservative added if applicable. Sample information will also be recorded in the field logbook.

#### **B3.3 Chain of Custody (COC)**

Proper sample handling and custody procedures ensure the custody and integrity of samples beginning at the time of sampling and continuing through transport, sample receipt, preparation, and analysis. A sample is in custody if it is in actual physical possession or in a secured area that is restricted to authorized personnel.

In the field, IDEQ and the Tribe fill out COC forms at the time of labeling the sample bottles (see Appendix C for a sample COC form). The COC form is used to document sample handling during transfer from the field to the laboratory and among contractors. The record of the physical sample (location and time of sampling) will be joined with the analytical results through accurate accounting of the sample custody. Sample custody applies to both field and laboratory operations. Analytical laboratory sample custody procedures are included in the laboratory QA plans or SOPs, which identify the roles of both the sample custodian and the laboratory coordinator. The list of items below should be included on the COC form.

1. Date and time of collection
2. Site identification
3. Sample matrix
4. Number of containers
5. Preservative used
6. Analysis required
7. Name of collector
8. Custody transfer signatures and dates and time of transfer
9. Name of laboratory admitting the sample

#### **B3.4 Sample Packaging and Shipping**

As samples are taken from the field back to the respective office-lab facilities of IDEQ and the Tribe, the following procedures are followed:

1. COC forms are checked for completeness, and copies are made for office records.

2. Sample containers are checked for tight and sealed lids, and that labels are secure.
3. Nutrient samples are stored overnight in a refrigerator; chlorophyll samples are stored in the freezer.
4. Trace metal samples are stored acidified at room temperature for up to one week.
5. Samples for trace metals are packaged and secured according to guidelines of the overnight shipping company selected. These samples are not required to be chilled during shipping. Chlorophyll samples will need to be packaged and shipped in dry ice. “Breathable containers”, specific for packages shipped in dry ice, are required and will be purchased by the Tribe and IDEQ. The White and Yellow copies of the EPA COC forms (Sample Custody & Analysis Required Form) are placed in the shipping containers. Labeling of packages will follow guidelines of the overnight carrier. Sample containers will be shipped for overnight delivery to the EPA Lab, Attn: Sample Custodian. IDEQ and the Tribe will try to coordinate efforts so that samples are shipped at the same time.
6. Samples for nutrient analysis will be hand delivered by IDEQ and the Tribe to their respective laboratories the morning after field sampling. Dissolved nitrite, nitrate, and ortho-phosphate have a 48 hour holding time before analysis.

#### **B4 ANALYTICAL METHODS**

Analytical methods for sample analysis are presented in **Table B-6**, along with target method detection limits, reporting limits, and quality control criteria (precision, accuracy, and completeness). Laboratory QA will be implemented and maintained according to the laboratory's QA plans and SOPs.

The analytical methods and associated QA/QC procedures were selected based on consideration of the project objectives. While a best effort will be made to achieve the project objectives, there may be cases in which it is not possible to meet the specified goals. Any limitation in data quality due to analytical problems (e.g. elevated reporting limits) will be identified within 48 hours and brought to the attention of the Tribe, IDEQ, and EPA QAO, as appropriate. In addition, this information will be discussed in the data evaluation report.

Procedures for laboratory analysis will be in accordance with procedures acceptable to the Tribe, IDEQ, and USEPA.

#### **B5 QUALITY CONTROL REQUIREMENTS**

This section describes the QC samples (e.g. field duplicates, blanks, and matrix spikes), data quality indicators, and associated measurement quality objectives (e.g. precision and accuracy goals). For field instrumentation used in this program, refer to sections B6 and B7 for QA/QC discussion and specifications.

## **B5.1 Quality Control Samples**

Field Quality Control (QC) and laboratory QC samples will be employed to evaluate data quality. QC samples are controlled samples introduced into the analysis stream whose results are used to review data quality and to calculate the accuracy and precision of the chemical analysis program. Collection and analysis frequency for field QC samples are generally recommended at a rate of 5 to 10 percent. Quality control criteria for laboratory analysis (measurement quality objectives) are listed in **Table B-6**.

QC procedures for the laboratory analysis will be consistent with the requirements described in the laboratories' protocols and methods. These requirements are defined in SOPs as part of the laboratory's QA program plan. All QC measurements and data assessment for this project will be conducted on samples from and within batches of samples from this project alone.

### **B5.1.1 Field Sampling Quality Control Requirements**

In general, and based on past studies, field QC efforts will emphasize detection of contamination and laboratory precision, primarily through the use of field contamination / equipment blanks, sample replicates, and field duplicates. Field contamination / equipment blanks are used to detect potential contamination. Lab-certified constituent-free water is put through all steps of the sampling and sample processing process and analyzed for the constituents of concern or interest. Sample replicates are used to evaluate laboratory precision – replicate sets of subsamples are withdrawn from the same churn-splitter volume and analyzed separately. Field duplicates are used to detect sampling method or *in situ* sample heterogeneity – one set of samples (from a specific depth, for example) is collected and processed, and then the process is repeated as close to the same time as possible (or simultaneously). A field contamination / equipment blank, sample replicate, or field duplicate QC sample will be collected on every sampling trip during this monitoring effort (see Table B-3).

Field Contamination Blanks A field blank is a sample of reagent water (certified contaminant free) placed in the water column sampler, and then transferred to the churn splitter. Non-filtered blank samples are placed in the proper laboratory sample bottles. A filtered blank sample is processed through the filter capsules, and then placed in the proper laboratory sample bottles. Field blank samples are preserved, sealed, handled, stored, shipped, and analyzed in the same manner as regular samples. The analysis of field blanks should yield values less than the reportable limits for each analyte (**Table B-6**). Values above the reportable limits may indicate sources of contamination from either the field monitoring environment and/or the laboratory environment.

At the beginning of each season of the monitoring program, before equipment and supplies are sent to the field, IDEQ and the Tribe will prepare equipment blanks in the respective office labs, and these blanks will be sent to the appropriate laboratories. A field blank will be prepared for each analyte listed in Table B-3. During the sample collection season, IDEQ and the Tribe will prepare field blanks, on the boat, 3 times throughout the sampling season for each analyte listed in Table B-3.

Sample Duplicates Duplicate sets of subsamples are withdrawn, from the same volume of water in the churn splitter. They are processed and analyzed separately to assess analytical precision. Prior to each sampling season, a schedule of sample duplicates is developed from the various sampling zone depths as shown in Table B-3. If the contracted laboratory also conducts sample duplicates, and reports the results, the frequency of field sample replicates shown may be reduced.

Field Duplicates A field duplicate is defined as a second sample from the same location and lake water column zone, collected in immediate succession, using identical techniques. A field duplicate provides estimates of the total sampling and analytical precision, and potential heterogeneity in the sampled medium. Duplicate samples are preserved, sealed, handled, stored, shipped, and analyzed in the same manner as the primary sample. Precision of duplicate results is calculated by the relative percent deviation (RPD), as defined in section B5.2. IDEQ and the Tribe will conduct field duplicate analysis from the euphotic zone composite samples at a rate shown in Table B-3 (around 10%).

Field Staff Duplicates Once a year, IDEQ and the Tribe will monitor a selected sampling site, side-by-side. The two monitoring boats will be anchored closely together at one of the program sampling sites, and then at the same time, conduct independently, all field measurements and water sample collections for submittal to the laboratory. Collected field data and laboratory data will be compared by the program managers for examination of differences, and where unacceptable differences exist, take corrective actions to ensure consistency.

### **B5.1.2 Laboratory Quality Control Samples**

Laboratory QC checks are accomplished by analyzing initial and continuing calibration samples, laboratory duplicate samples, method blanks, matrix spikes, laboratory control samples, and standard reference materials. Not all of these QC samples will be required for all methods. Laboratory QC sample results are reported with the sample data reports.

Initial and Continuing Calibration Samples Laboratory instrument calibration requirements are summarized in the laboratory SOPs.

Laboratory Duplicate Precision of the analytical system is evaluated by using laboratory duplicates. Laboratory duplicates are two portions of a single homogeneous sample analyzed for the same parameter.

Method Blank Method (preparation) blanks are used to check for laboratory contamination and instrument bias. A method blank is an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing, and analyzed with each batch. The method blank is carried through the complete sample preparation and analytical procedure. QC criteria require that no contaminants be detected in the blank(s) above the method quantitative limit (reporting limit). If a chemical is detected, the action taken will follow the laboratory SOPs.

Matrix Spike/Matrix Spike Duplicates (MS/MSDs) MS/MSDs are used to assess sample matrix interferences and analytical errors, as well as to measure the accuracy and precision of the

analysis. For the Coeur d'Alene Lake monitoring effort described in this QAPP, QC samples of this type will be prepared by and in the laboratory, as opposed to in the field by IDEQ and Tribal sampling staff. For MS or MSD samples, known concentrations of analytes are added to the environmental samples prior to digestion or preparation. The samples are then processed through the entire analytical procedure and the recovery of analytes is calculated. The spiked concentration must be greater than 25% of the unspiked concentration in the sample. Results are expressed as percent recovery of the known spiked amount for MSs and the relative percent difference (RPD) for MSDs. A frequency of 1 MS/MSD in each group of 20 samples is recommended.

Because MS/MSD samples measure the matrix interference of a specific matrix, samples designated for analysis as MS/MSD samples are project specific. The laboratory may not substitute a sample from another project to act as the QC sample for the analytical batch containing samples from this project. The MS/MSD samples will be analyzed for the same parameters as the associated field samples in the same QC analytical batch.

Laboratory Control Samples/Laboratory Control Sample Duplicates (LCS/LCSDs) LCS is a clean matrix spiked with known quantities of analytes. The LCS is processed with field samples through every step of preparation of analyses. Measuring percent recovery of each analyte in the LCS provides a measure of accuracy for the analyte in the project samples. The EPA lab does LCS duplicates, and the LCS %Rec pairs can be matched to calculate a %RPD precision. For nutrients, SVL Analytical and Tshimakain Creek Laboratory do not perform LCS duplicates.

Standard Reference Materials SRMs are used to monitor the laboratory's day-to-day performance of routine analytical methods, independent of matrix effects. The SRMs are extracted and analyzed with each batch of samples. Results are compared on a per-batch basis to established control limits and are used to evaluate laboratory performance for precision and accuracy. Laboratory control samples may also be used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false-positive measurements.

## **B5.2 Analytical Quality Indicators**

Project-specific control limits (measurement quality objectives) for these parameters are presented in **Table B-6**.

### **B5.2.1 Precision**

Precision is defined as the degree of agreement between independent, similar, or repeated measures. Precision is expressed in terms of analytical variability. For this project, analytical variability will be measured as the RPD or coefficient of variability between analytical field and laboratory duplicates, and between the MS and MSD analysis. The field duplicates incorporate both monitoring and laboratory variability, while the laboratory duplicates isolate analytical variability.

Precision will be calculated as the RPD as follows:

$$\% RPD_i = \frac{2|O_i - D_i|}{(O_i + D_i)} \times 100\%$$

where:

$\%RDP_i$  = relative percent difference for compound  $i$   
 $O_i$  = value of compound  $i$  in original sample  
 $D_i$  = value of compound  $i$  in duplicate sample

The resultant laboratory RPD will be compared to acceptance criteria, and deviations from specified limits will be reported. If the objective criteria are not met, the laboratory will supply a justification of why the acceptability limits were exceeded and implement the appropriate corrective actions. If a laboratory RDP is within acceptance criteria, but a field RDP is not, IDEQ and Tribe project managers will examine field procedures for duplicates and seek a cause. The RPDs will be reviewed during data quality review, and deviations from the specified limits will be noted and the effect on reported data commented upon by the data reviewers.

### B5.2.2 Accuracy

Accuracy is the amount of agreement between a measured value and the true value. It will be measured as the percent recovery of MS/MSD, and standard reference samples. Additional potential bias will be quantified by the analysis of method blank samples.

Accuracy will be calculated as percent recovery of analytes as follows:

$$\% R_i = (Y_i \div X_i) \times 100\%$$

where:

$\%R_i$  = percent recovery for compound  $i$   
 $Y_i$  = measured analyte concentration in sample  $i$   
(measured concentration minus original sample concentration)  
 $X_i$  = known analyte concentration in sample  $i$

The resultant percent recoveries will be compared to acceptance criteria, and deviations from specified limits will be reported. If the objective criteria are not met, the laboratory will supply a justification of why the acceptability limits were exceeded and implement the appropriate corrective actions. Percent recoveries will be reviewed during data quality review, and deviations from the specified limits will be noted and the effect on reported data commented upon by the data reviewers.

### B5.2.3 Completeness

Completeness for usable data is defined as the percentage of usable data obtained from the total amount of data generated. Because the number of samples that will be collected to measure each parameter exceeds that required for the analysis, approximately 100 percent completeness is anticipated. When feasible, the amount of sample collected will be sufficient to reanalyze the sample, should the initial results not meet QC requirements. Less than 100 percent completeness could result if sufficient chemical contamination exists to require sample dilutions, resulting in an increase in the project-related detection/quantitation limits for some parameters. Highly contaminated environments can also be sufficiently heterogeneous to prevent the achievement of

specified precision and accuracy criteria. The target goal for completeness shall be 95% for all data. Quality data are data obtained in a sample batch for which all QC criteria were met. Completeness will be calculated as follows:

$$\%C = \frac{A}{I} \times 100\%$$

where:

$\%C$  = percent completeness (analytical)  
 $A$  = actual number of samples collected/valid analyses obtained  
 $I$  = intended number of samples/analyses requested

Non-valid data (i.e. data qualified as “R” rejected) will be identified during the QA review.

#### **B5.2.4 Representativeness**

Representativeness is the degree to which sample results represent the system under study. This component is generally considered during the design phase of a program. This program will use the results of all analyses to evaluate the data in terms of their intended use.

#### **B5.2.5 Comparability**

Comparability is the degree to which data from one study can be compared with data from other similar studies (e.g. comparing with USGS Coeur d'Alene Lake studies in 1990-94 and 2004 – 2006), reference values (such as background), reference materials, and screening values. This goal will be achieved through using standard techniques to collect and analyze representative samples and reporting analytical results in appropriate units.

#### **B5.2.6 Sensitivity**

The sensitivity of the analytical methods (i.e. quantitation limits) identified for this project is sufficient to allow comparison of project results to design criteria. Analytical method reporting limits for all requested analytes are listed in **Table B-6**.

### **B5.3 Failures in Quality Control and Corrective Action**

Throughout the sampling season, IDEQ and Tribe program managers will communicate on their review of field and laboratory QC results following the receipt of laboratory data reports. There would also be communication with the Laboratory QA manager involving unsatisfactory results from the laboratory QC samples. Consultations are made for recommended measures to find a cause and rectify unsatisfactory QC results.

Differences in field duplicate sample results are used to assess the entire sampling process, including environmental variability, and field duplicate samples are compared with sample and laboratory duplicates. Professional judgment will be relied upon in evaluating results and rejecting results based on wide variability is a possibility.

If an analyte concentration in a field blank is reported above the method quantitative limit (reporting limit), the Tribe and IDEQ will attempt to rectify the cause of contamination by examining the laboratory data record of method blanks, re-examining equipment cleaning and handling procedures, and/or conducting “isolate tests” of field equipment, including laboratory sample bottles.

All information of field and laboratory QC results will be documented and presented in program reports.

## **B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS**

Preventative maintenance will take two forms: (1) implementing a schedule of preventive maintenance activities to minimize downtime and ensure accuracy of measurement systems, and (2) ensuring a stock of critical spare parts and backup systems and equipment. The preventive maintenance approach for specific pieces of equipment used in sampling, monitoring, and documentation will follow manufacturer specifications and method requirements. Performance of these maintenance procedures will be documented in field logbooks and laboratory notebooks.

IDEQ and the Tribe will perform testing, inspection, and maintenance of the Li-Cor<sup>®</sup> surface incident solar radiation measurement system, the Hydrolab<sup>®</sup> DS5 submersible multiparameter water quality instrumentation, and the peristaltic pump (Tribe)/vacuum aspirator (IDEQ) and associated filtration apparatus for water and chlorophyll samples. This maintenance will be performed prior to each sampling visit (during calibration) following the manufacturer's instructions.

In addition, IDEQ and the Tribe send field instruments to the manufacturer for factory maintenance and calibration at frequencies recommended by the manufacturer (annually or at least once every two years).

All laboratories will have service contracts in place for measurement systems that are used to measure project samples. Each laboratory will follow the preventive maintenance procedures specified in approved SOPs.

## **B7 INSTRUMENT CALIBRATION AND FREQUENCY**

The day prior to each sampling visit, IDEQ and the Tribe will calibrate their respective Hydrolab<sup>®</sup> DS5 units in the lab for specific conductance, dissolved oxygen (IDEQ and the Tribe now calibrate in the lab the day of sampling), turbidity, pH, and chlorophyll *a* fluorescence according to the manufacturer's instructions. At the beginning, middle, and end of the sampling season, IDEQ will also test lab-bench calibrations of dissolved oxygen (mg/L) with a Winkler titration method and will test water temperature readings with a water bath method using a lab grade thermometer. The Tribe will attempt to do so simultaneously with IDEQ at the IDEQ's facilities.

Calibration and frequency of calibration of laboratory instruments will be according to the requirements of each method of analysis. These requirements are listed in the laboratory SOPs that describes how each target compound will be measured.

## **B8 INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND CONSUMABLES**

Supplies and consumables shall be inspected and accepted for use by the agency ordering the supplies. IDEQ and Tribal staff are responsible for ordering and inspecting the supplies that are required to successfully accomplish the lake monitoring program. These personnel will inspect and accept or deny the delivery of supplies and consumables.

Supplies and reagents needed by IDEQ and the Tribe include those listed in Table B-5 (laboratory sample bottles, filters, and chemicals for preservation). A complete list with specifications is listed in Appendix B.

Based on advice from the EPA Manchester Lab, a supplier has been identified to purchase PreCleaned Certified™ Procedure 3, 500 mL sample bottles for dissolved and total metals analysis (Environmental Sampling Supply, ESS). Container preparation includes: phosphate-free detergent washing, multiple tap water and ASTM Type I deionized water rinses, and 1:1 HNO<sub>3</sub> rinses. Sample bottles are then oven dried and capped. DEQ also purchases PreCleaned Certified™ Procedure 2 500 mL sample bottles for dissolved nitrate. Container preparation includes phosphate-free detergent washing and multiple tap water and ASTM Type I deionized water rinses. Containers are oven dried and capped. Corning 50 mL sterile centrifuge tubs are used for dissolved ammonia sample.

In early spring of 2011, IDEQ purchased a Millipore Milli-Q® Integral Water Purification System. The Millipore Milli-Q® System produces Type 1 (Ultra-Pure Blank Water), which is suitable for Inorganic Blank Water (USGS terminology) used in equipment and field blanks. Equipment blanks will be prepared at our respective office labs and submitted to EPA prior to the initial field sampling trip. This blank testing will also include the analytical grade sulfuric and nitric acid, purchased in vials, for sample preservation.

Deionized water will be obtained from the Tshimakain Creek Laboratory (Tribe) and IDEQ will produce its own deionized water in-house using the Millipore Milli-Q® Integral Water Purification System. Cleaning rinses made with this deionized water will be tested in the equipment blank samples submitted both to EPA for metals and the other two laboratories for nutrients. Starting in 2011 IDEQ will conduct a 5% HCl rinse - DIW rinse of the 4 L and 10 L carboys on a regular basis.

## **B9 DATA ACQUISITION REQUIREMENTS**

During this project, data may be obtained from indirect measurement sources, such as visual observations, computer printouts, and literature searches. Monitoring and research data may also be obtained from agencies conducting work within the Coeur d'Alene Basin such EPA, USGS, U.S. Forest Service, U.S. Fish & Wildlife Service, University of Idaho, and Idaho Department of Fish & Game. The sources of these data will be recorded and the quality of the data will be assessed to determine if the data are consistent with project objectives and appropriate for supporting a specific decision. Usability or limitations of data, such as representativeness, bias, and precision will be discussed, and any uncertainty will be assessed prior to the inclusion of the data in the decision making process.

In particular, IDEQ and the Tribe will obtain data from the Coeur d'Alene Basin Environmental Monitoring Program (BEMP) which is operated by USGS for EPA in support of Superfund remediation activities ongoing and planned throughout the Coeur d'Alene Lake / Spokane River Basin (USEPA 2003). Water quality data for the inflow and outflow tributaries will undoubtedly be compared with in-lake data collected in this monitoring effort and will continue to be integrated into ELCOM-CAEDYM modeling efforts.

## **B10 DATA MANAGEMENT**

Physical measurement data collected from the Hydrolab<sup>®</sup> DS5 is processed and recorded electronically through an on-board lap-top computer run with the Hydras 3 LT software. This water column profile data are stored in Excel spreadsheet files. At the same time, parameter readings at each depth of the profile are recorded manually on a field form (Appendix A). The standard procedure for ensuring proper recording of data is for one field member to state the parameter values read from the computer screen, while another field member records the data manually, repeating the value as it is written down. The same procedure is used for recording underwater light readings from the LiCor<sup>®</sup> 1400; one staff member reading values from the data logger screen, another staff member repeating the values as they are written down on a field form. Double checking in the field is also done for GPS readings and Secchi disc measurements.

Back at the office, the Hydrolab<sup>®</sup> and LiCor<sup>®</sup> 1400 field data files are downloaded onto a desktop computer which has proper backup procedures. The field data files are checked against the profile field forms. Other field collected information which is recorded only manually (Secchi disc, etc.) are entered into Excel spreadsheets on a desktop computer. One staff member key-punches the data in, and then afterwards, the other staff member checks these numbers with the data on the field forms or field logbook.

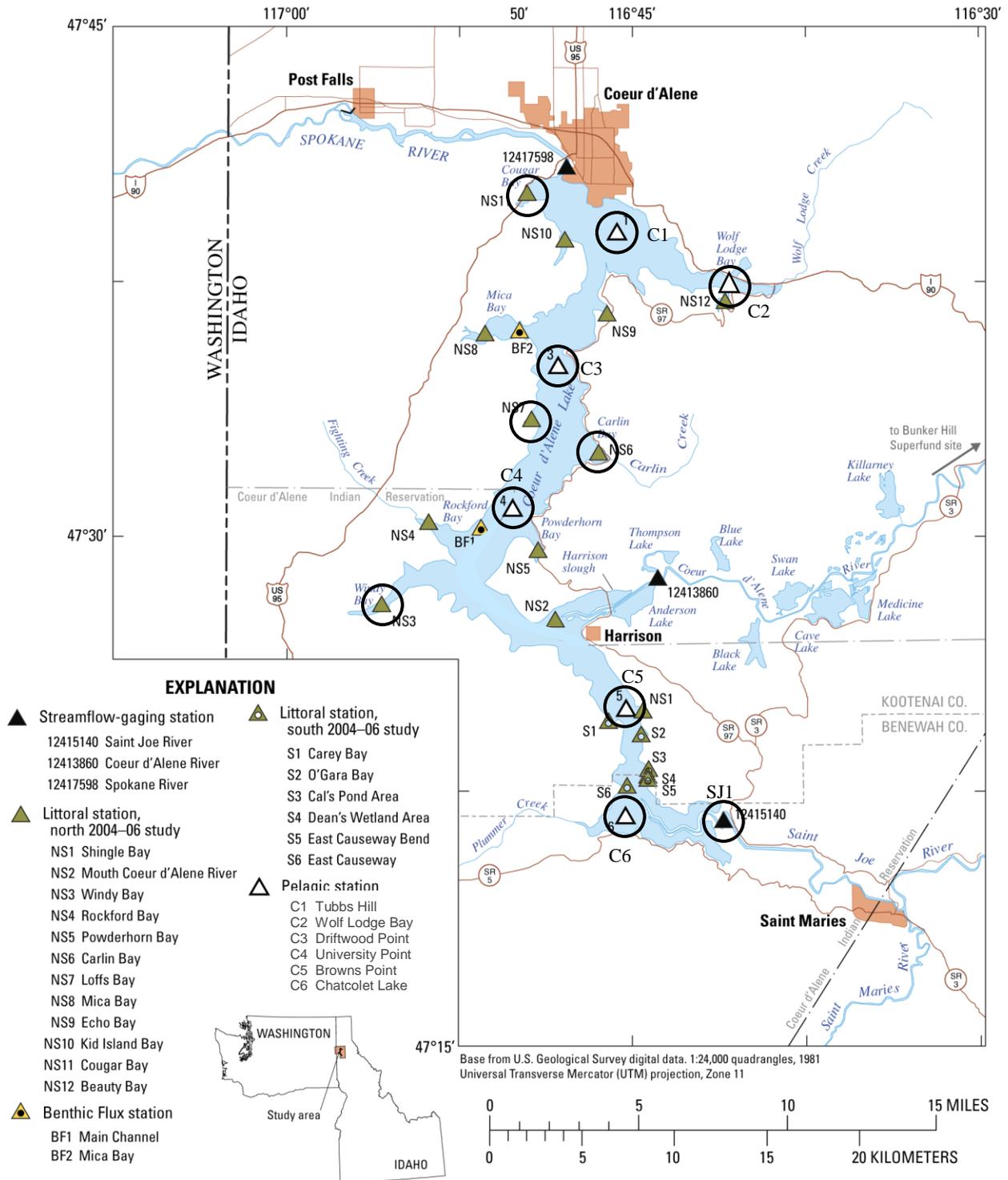
Laboratory results data are normally received through hard-copy. This data is entered into Excel spreadsheets established for the lake monitoring program. Afterwards, the other staff member checks the entered numbers with the hard-copy laboratory sheets. For both field collected data and laboratory results data, the Tribe and IDEQ will exchange electronic files.

The management of data also includes all mathematical operations and analyses performed on data as collected, to change the form, location, quantity, or dimension of data. Technical data management guidance includes the following:

- ensuring that data encoding and entry into databases is correct, including data validation/review criteria and overall project data validation (see above)
- converting data into related values, including the conversion of calibration readings into an equation that can be applied to measurement readings
- transmitting data, either hard copy or electronic, without error
- reducing data (including calculations) with an associated loss of detail or number

- analyzing data by applying statistics, standard error, confidence intervals, and model parameters
- tracking the flow of the data through the data processing system
- ensuring secure storage and timely retrieval of data

IDEQ and the Tribe will be manipulating, assessing, and displaying the collected data in many ways, including: calculation of central tendency statistics, box plots, statistical trend analysis, profile graphs, and input to ELCOM-CAEDYM model runs.



**Figure B-1. Map of sampling sites for the 2011 Coeur d'Alene Lake Monitoring Program (circled); map provided by USGS for WY04-06 sampling program (Wood and Beckwith, 2008)**

**Table B-1. Sampling Locations of the 2011 Coeur d'Alene Lake Monitoring Program**

<b>USGS Site #</b>	<b>USGS site number, location, and approximate depth</b>	<b>Latitude</b>	<b>Longitude</b>
C1	473900116453000 Coeur d'Alene Lake – 1.3 miles southeast of Tubbs Hill near Coeur d'Alene, ID - depth: 40 meters*	47° 39' 00"	-116° 45' 30"
C2	473730116410000 Coeur d'Alene Lake – at Wolf Lodge Bay near Coeur d'Alene, ID - depth: 29.5 meters	47° 37' 30"	-116° 41' 00"
C3	473500116482000 Coeur d'Alene Lake – 0.8 miles southwest of Driftwood near Coeur d'Alene, ID - depth: 52.0 m	47° 35' 00"	-116° 48' 20"
C4	473054116500600 Coeur d'Alene Lake – 1.7 miles northeast of University Point near Harrison, ID - depth: 40 meters	47° 30' 54"	-116° 50' 06"
Windy Bay	472750116555900Coeur d'Alene Lake – Windy Bay - depth: To be determined	To be determined	To be determined
Carlin Bay	473615116510000 Coeur d'Alene Lake –Carlin Bay- depth: To be determined	To be determined	- To be determined
Loffs Bay	473018116531800 Coeur d'Alene Lake – Loffs Bay - depth: To be determined	To be determined	To be determined
Cougar Bay	Coeur d'Alene Lake – Cougar Bay - depth: To be determined	To be determined	To be determined
C5	472500116450000 Coeur d'Alene Lake – mid lake between Browns Point and north end of Shingle Bay near Harrison, ID Depth: 17 meters*	47° 25' 00"	-116° 45' 00"
C6	472120116451000 Chatcolet Lake 0.4 miles northwest of Rocky Point near Plummer, ID = depth: 11 m	47° 21' 20"	-116° 45' 10"
SJ1	Lower St. Joe River - ~100 m upstream of USGS gage 12415140 near Chatcolet, ID Depth: 18 meters*	47° 21' 27"	-116° 41' 10"

Datum NAD 1927

At full summer pool, lake surface elevation 2128 feet

**Table B-2. Annual Sampling Visits for the Coeur d'Alene Lake Monitoring Program  
 (Selection of 8 sampling events below)**

<b>Sampling visits</b>	<b>Season</b>	<b>Month</b>	<b>Lake condition</b>
1	winter - early spring	December - March	<i>Variable schedule:</i> unstratified; prior to spring peak runoff; potential opportunity to sample during major rain-on-snow lake inflow event.
2	winter - early spring	January - March	<i>Optional schedule:</i> unstratified; prior to spring peak runoff; second opportunity to sample during major rain-on-snow lake inflow event or early spring peak runoff.
3	spring	late March – early June	<i>Variable schedule:</i> during spring peak runoff: opportunity to sample strong riverine influences on the lake; spring pulse of diatom growth develops.
4	late spring	mid-June	<i>Set schedule:</i> onset of stratification: spring pulse of diatom growth; before the onset of strong thermal stratification.
5	summer	mid-July	<i>Set schedule:</i> strong thermal stratification is established; sample the development of a metalimnetic chlorophyll <i>a</i> maximum; for some years, the peak of epilimnetic temperatures and thermocline thickness.
6	summer	mid-August	<i>Set schedule:</i> for some years, the peak of epilimnetic temperatures and thermocline thickens; declines in dissolved oxygen near bottom may become evident; phytoplankton peaks might start to develop at stations C5 and C6.
7	late summer	mid-September	<i>Optional – depending on early season sampling:</i> phytoplankton growth waning in northern pool; still-strong thermal stratification in northern pool; DO deficit at C5 may be at maximum for season.
8	fall	early-October	<i>Set schedule:</i> within northern pool, thermocline is deep but stratification still persists; DO deficits near bottom are still evident and often exhibit the peak of DO deficit for the season; waters of C5 and C6 have undergone fall turnover, and phytoplankton growth may still be at its peak.
9	early winter	late-November or early December	<i>Set schedule:</i> unstratified (lake has undergone fall turnover); water quality data fairly uniform from top to bottom and not yet affected by a rain-on-snow event (usually).

**Table B-3. Number of Samples of Chemical Constituents Needed for IDEQ / Tribe Coeur d'Alene Lake Monitoring Program**

Former USGS stations sampled	Constituents	Annual No. of samples (sites*visits)	Total No. of field QC replicate samples
<b>Euphotic Zone Composite</b>			
C1, C2, C3, C4, Windy, Carlin, Loffs, Cougar, C5, C6, SJ1	<b><u>Nutrients:</u></b>	11 sites, 8 samplings/year	1 Field replicate at each of 11 sites in sampling year
	ammonia, dissolved (filtered, 0.45 µm), as N	88	11
	nitrite (Tribe) and nitrate, dissolved (filtered, 0.45 µm), as N	88	11
	total nitrogen (nitrite+nitrate+ammonia+organic-N) or TKN, as N	88	11
	total phosphorus, as P	88	11
	total (filtered, 0.45 µm) dissolved P, as P	88	11
	dissolved ortho-P, as P	88	11
	<b><u>Metals:</u></b>		
	arsenic, total	88	11
	cadmium, total	88	11
	lead, total	88	11
	zinc, total	88	11
	iron, total	88	11
	manganese, total	88	11
	arsenic, filtered (0.45 µm & 0.20 or 0.10 µm)	103	11
	cadmium, filtered (0.45 µm & 0.20 or 0.10 µm)	103	11
	lead, filtered (0.45 µm & 0.20 or 0.10 µm)	103	11
	zinc, filtered (0.45 µm & 0.20 or 0.10 µm)	103	11
	iron, filtered (0.45 µm & 0.20 or 0.10 µm)	103	11
	manganese, filtered (0.45 µm & 0.20 or 0.10 µm)	103	11
	<b><u>Minerals:</u></b>		
total hardness, as CaCO <sub>3</sub>	88	11	
calcium, filtered (0.45 µm & 0.20 or 0.10 µm)	103	11	
magnesium, filtered (0.45 µm & 0.20 or 0.10 µm)	103	11	
<b><u>Biological:</u></b>			
chlorophyll <i>a</i>	88	11	
phytoplankton identification & enumeration	88	1	

**Table B-3 Continued**

Former USGS stations sampled	Constituents	Annual No. of samples (sites*visits)	Total No. of field QC replicate samples
<b>Discrete samples during flood flow conditions and at summer chlorophyll <i>a</i> maximums</b>			
C1, C2, C3, C4, C5, Windy, Carlin, Loffs, Cougar	<b><u>Nutrients:</u></b>	5 sites, 4 times/year 4 bays, 2 times/year	Sample replicate
	ammonia, dissolved (filtered, 0.45 µm), as N	28	2
	nitrite (Tribe) and nitrate, dissolved (filtered, 0.45 µm), as N	28	2
	total nitrogen (nitrite+nitrate+ammonia+organic-N) or TKN, as N	28	2
	total phosphorus, as P	28	2
	total (filtered, 0.45 µm) dissolved P, as P	28	2
	dissolved ortho-P, as P	28	2
	<b><u>Metals:</u></b>		
	arsenic, total	28	2
	cadmium, total	28	2
	lead, total	28	2
	zinc, total	28	2
	iron, total	28	2
	manganese, total	28	2
	arsenic, filtered (0.45 µm & 0.10 µm)	30	2
	cadmium, filtered (0.45 µm & 0.10 µm)	30	2
	lead, filtered (0.45 µm & 0.10 µm)	30	2
	zinc, filtered (0.45 µm & 0.10 µm)	30	2
	iron, filtered (0.45 µm & 0.10 µm)	30	2
	manganese, filtered (0.45 µm & 0.10 µm)	30	2
	<b><u>Minerals:</u></b>		
	total hardness, as CaCO <sub>3</sub>	28	2
	calcium, filtered (0.45 µm)	30	2
magnesium, filtered (0.45 µm)	30	2	
<b><u>Biological:</u></b>			
chlorophyll <i>a</i>	10	1	
phytoplankton identification & enumeration	10	0	

**Table B-3 Continued**

Former USGS stations sampled	Constituents	Annual No. of samples (sites*visits)	Total No. of field QC replicate samples
<b>Discrete samples at 20 m (when chl <i>a</i> max not taken) and 30 m</b>			
C1, C2 (20 m only), C3, C4	<p><b><u>Nutrients:</u></b>                      ammonia, dissolved (filtered, 0.45 µm), as N                      nitrate, dissolved (filtered, 0.45 µm), as N                      total nitrogen (nitrite+nitrate+ammonia+organic-N), as N                      total phosphorus, as P                      total (filtered, 0.45 µm) dissolved P, as P                      dissolved ortho-P, as P</p> <p><b><u>Metals:</u></b>                      arsenic, total                      cadmium, total                      lead, total                      zinc, total                      iron, total                      manganese, total</p> <p>arsenic, filtered (0.45 µm &amp; 0.10 µm)                      cadmium, filtered (0.45 µm &amp; 0.10 µm)                      lead, filtered (0.45 µm &amp; 0.10 µm)                      zinc, filtered (0.45 µm &amp; 0.10 µm)                      iron, filtered (0.45 µm &amp; 0.10 µm)                      manganese, filtered (0.45 µm &amp; 0.10 µm)</p> <p><b><u>Minerals:</u></b>                      total hardness,                      calcium, filtered (0.45 µm &amp; 0.10 µm)                      magnesium, filtered (0.45 µm &amp; 0.10 µm)</p>	<p>3 sites, 2 depths, and 1 site, 1 depth 6 times/year</p> <p>42 42 42 42 42 0 42 42 42 42 42 42 46 46 46 46 46 46 42 46 46</p>	<p>Field replicates and Sample replicates</p> <p>5 5 5 5 5 0 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5</p>

**Table B-3 Continued**

Former USGS stations sampled	Constituents	Annual No. of samples (sites*visits)	Total No. of field QC replicate samples
<b>Discrete samples 1 meter off bottom</b>			
C1, C2, C3, C4, C5, C6, SJ1	<b><u>Nutrients:</u></b>	7 sites, 8 samplings / year	1 Sample replicate at each of 10 sites in sampling year
	ammonia, dissolved (filtered, 0.45 µm), as N		10
	nitrite (Tribe) and nitrate, dissolved (filtered, 0.45 µm), as N		10
	total nitrogen (nitrite+nitrate+ammonia+organic-N) or TKN, as N		10
	total phosphorus, as P		10
	total (filtered, 0.45 µm) dissolved P, as P		10
	dissolved ortho-P, as P		0
	<b><u>Metals:</u></b>		
	arsenic, total		10
	cadmium, total		10
	lead, total		10
	zinc, total		10
	iron, total		10
	manganese, total		10
	arsenic, filtered (0.45 µm & 0.10 µm)		10
	cadmium, filtered (0.45 µm & 0.10 µm)		10
	lead, filtered (0.45 µm & 0.10 µm)		10
	zinc, filtered (0.45 µm & 0.10 µm)		10
	iron, filtered (0.45 µm & 0.10 µm)		10
	manganese, filtered (0.45 µm & 0.10 µm)		10
<b><u>Minerals:</u></b>			
total hardness, as CaCO <sub>3</sub>	10		
calcium, filtered (0.45 µm & 0.10 µm)	10		
magnesium, filtered (0.45 µm & 0.10 µm)	10		

**Table B-3 Continued**

<b>Field Contamination (equipment) Blanks</b> Lab-certified contaminant-free water		<b>Total No. of field QC samples - blanks</b>
	8 x 4 L jugs needed	IDEQ and Tribe each: -in lab before first sampling trip At end of: -first sampling trip -mid-July trip -early October trip
<b><u>Nutrients:</u></b>		
ammonia, dissolved (filtered, 0.45 µm), as N		8
nitrite (Tribe) and nitrate, dissolved (filtered, 0.45 µm), as N		8
total nitrogen (nitrite+nitrate+ammonia+organic-N) or TKN, as N		8
total phosphorus, as P		8
total (filtered, 0.45 µm) dissolved P, as P		8
dissolved ortho-P, as P		8
<b><u>Metals:</u></b>		
arsenic, total		8
cadmium, total		8
lead, total		8
zinc, total		8
iron, total		8
manganese, total		8
arsenic, filtered (0.45 µm & 0.20 or 0.10 µm)		10
cadmium, filtered (0.45 µm & 0.20 or 0.10 µm)		10
lead, filtered (0.45 µm & 0.20 or 0.10 µm)		10
zinc, filtered (0.45 µm & 0.20 or 0.10 µm)		10
iron, filtered (0.45 µm & 0.20 or 0.10 µm)		10
manganese, filtered (0.45 µm & 0.20 or 0.10 µm)		10
<b><u>Minerals:</u></b>		
total hardness, as CaCO <sub>3</sub>		8
calcium, filtered (0.45 µm & 0.20 or 0.10 µm)		10
magnesium, filtered (0.45 µm & 0.20 or 0.10 µm)		10
<b><u>Biological:</u></b>		
chlorophyll <i>a</i> ,		8



**Table B-5. Water Sample Containers, Preservation, and Holding Times**

Analysis	Container Size	Container Type	Preservation	Holding Times
total phosphorus	250 mL	opaque polyethylene	H <sub>2</sub> SO <sub>4</sub> to pH<2, cool to ≤6°C	28 days
total dissolved phosphorus	250 mL	opaque polyethylene	H <sub>2</sub> SO <sub>4</sub> to pH<2, cool to ≤6°C	28 days
dissolved ortho-phosphate	250 mL	opaque polyethylene	cool to ≤6°C	48 hours
total nitrogen (IDEQ)	40 mL (2)	glass	HCl to pH<2, cool to ≤6°C	28 days
total Kjeldahl nitrogen (Tribe)	500 mL	opaque polyethylene	H <sub>2</sub> SO <sub>4</sub> to pH<2, cool to ≤6°C	28 days
dissolved ammonia	50 mL	polypropylene	H <sub>2</sub> SO <sub>4</sub> to pH<2, cool to ≤6°C	28 days
dissolved nitrate (Tribe and IDEQ) and dissolved nitrite(Tribe)	500 mL	opaque polyethylene	cool to ≤6°C	48 hours
total metals cadmium, lead, zinc, arsenic, iron, manganese, hardness	500 mL	certified clean, pre-acid rinsed opaque polyethylene	HNO <sub>3</sub> to pH<2 unchilled	6 months
dissolved metals cadmium, lead, zinc, arsenic, iron, manganese, calcium, magnesium	500 mL	certified clean, pre-acid rinsed opaque polyethylene	HNO <sub>3</sub> to pH<2 unchilled	6 months
chlorophyll <i>a</i>	50 mm	petri dish foil covered	3 drops MgCO <sub>3</sub> dry ice	6 months
phytoplankton ID & enumeration	125 ml	brown polyethylene	1.5 ml Lugol's solution	6 months
filters for dissolved nutrients & metals	0.45 µm pore size	capsule filters		
post filters for dissolved metals (Tribe)	0.20 µm pore size	membrane filters		
post filters for dissolved metals (IDEQ)	0.10 µm pore size	Polyethersulphone (PES) membrane filters		
filters for chlorophyll <i>a</i>	0.3 µm pore size	glass fiber filter		
H <sub>2</sub> SO <sub>4</sub> vials certified contaminant free	0.5 mL	glass ampules /Poly Vials		
HNO <sub>3</sub> vials certified contaminant free	1 mL	glass ampules/Poly Vials		
bulk certified contaminant free HCl for 5% cleaning solutions	2.5 L	glass		
certified contaminant free blank water	20 L	clear polyethylene		
deionized water for cleaning rinses	4 L carboys	opaque polyethylene		

**Table B-6. Analytical Methods and Data Quality for Analytes of the Coeur d'Alene Lake Monitoring Program (NOTE: Target reporting limits are the values used by the EPA Manchester Lab, Spokane Tribal Lab, and SVL Analytical for the 2007 monitoring year)**

Analyte	Analytical Method	Target reporting limit	Precision & Accuracy/ completeness
<b>Nutrients</b>			
<i>TCL / SVL Analytical</i>		<i>TCL / SVL</i>	
ammonia, dissolved <sup>(a)</sup>	EPA 350.3 (Tribe & DEQ TCL Lab)	10 µg/L	+/- 25% 95%
nitrite, dissolved <sup>(a)</sup>	EPA 300.0 (Tribe TCL Lab)	10 µg/L	
nitrate, dissolved <sup>(a)</sup>	EPA 300.0 (Tribe & DEQ TCL Lab)	10 µg/L	
total nitrogen	SVL = SM <sup>b</sup> D-5176	50 µg/L	
total Kjeldahl nitrogen	TCL= EPA 351.2	50 µg/L	
total phosphorus	EPA 365.3 / SM 4500-P-E	5 / 3 µg/L	
total dissolved phosphorus <sup>(a)</sup>	EPA 365.3 / SM 4500-P-E	5 / 3 µg/L	
orthophosphate, dissolved <sup>(a)</sup>	EPA 365.5 / SM 4500-P-E	2 / 3 µg/L	
<b>Total recoverable metals, unfiltered, digested</b>			
<i>EPA Manchester Lab</i>			
cadmium	EPA 200.8 – ICP-MS	0.13 µg/L	+/- 25% 95%
lead	EPA 200.8 – ICP-MS	0.13 µg/L	
zinc	EPA 200.7 – ICP-SAS	5.0 µg/L	
arsenic	EPA 200.8 – ICP-MS	0.63 µg/L	
iron	EPA 200.7 – ICP-SAS	5.0 µg/L	
manganese	EPA 200.8 – ICP-MS	0.13 µg/L	
<b>Dissolved metals, filterable, undigested<sup>(a)</sup></b>			
<i>EPA Manchester Lab</i>			
cadmium	EPA 200.8 – ICP-MS	0.10 µg/L	+/- 25% 95%
lead	EPA 200.8 – ICP-MS	0.10 µg/L	
zinc	EPA 200.7 – ICP-SAS	5.0 µg/L	
arsenic	EPA 200.8 – ICP-MS	0.20 µg/L	
iron	EPA 200.7 – ICP-SAS	5.0 µg/L	
manganese	EPA 200.8 – ICP-MS	0.10 µg/L	
<b>Minerals</b>			
<i>EPA Manchester Lab</i>			
total hardness (as CaCO <sub>3</sub> )	SM 2340B	0.30 mg/L	
calcium, dissolved	EPA 200.7 – ICP-AES - mod. scan	30 µg/L	+/- 25%
magnesium, dissolved	EPA 200.7 – ICP-AES - mod. scan	50 µg/L	95%
<b>Biological</b>			
<i>EPA Manchester Lab</i>			
chlorophyll <i>a</i>	SM 1002G – fluorometric	1.0 µg/L	+/- 25% 95%
<b>Biological</b>			
<i>TG Eco-Logic</i>			
phytoplankton	SM 1002 C-F – identification /enumeration with sedimentation and 1500 magnification	n/a	n/a

a = Samples will be field filtered through a 0.45 µm pore size capsule filter for dissolved analysis  
b = Standard Methods for the Examination of Water and Wastewater

## **PART C. ASSESSMENT AND OVERSIGHT**

### **C1 ASSESSMENTS AND RESPONSE ACTIONS**

This section identifies assessment and reporting activities that will be involved in this program. The activities include independent technical reviews of the monitoring work plan and reports, field readiness reviews, data quality assessments, annual and five-year reports, and corrective actions of QA nonconformance. IDEQ and Tribe program managers, as well as the laboratory QA manager, are responsible for assessments and response actions.

#### **C1.1 Independent Technical Reviews**

The USEPA, as a financial partner in the Coeur d'Alene Lake Monitoring Program, provides initial independent technical review by having input and approving this QAPP, and then on a continuing basis by review and comment of annual and five-year project reports.

The existing Technical Leadership Group (TLG), assigned as a technical advisory committee to the BEIPC, will provide independent technical review of the lake monitoring work plan (as incorporated within this QAPP), along with review of annual and five-year reports of the monitoring program. The TLG includes technical staff from a wide array of governmental and tribal agencies (including USEPA), along with representatives from citizen groups who have involved themselves with technical issues. The TLG often provides technical discussion and input to scientific endeavors within the Coeur d'Alene Basin, including projects funded by CWA 104(b)(3) grant awards.

IDEQ and the Tribe will offer independent review of each other's field procedures, handling of data, and examination of laboratory data reports. There will be frequent communication between the staffs of IDEQ and the Tribe.

#### **C1.2 Data Quality Assessments**

Program managers for IDEQ and the Tribe are responsible for preparing data quality assessments to document the overall quality of data collected and of established quality criteria/indicators. The data assessment parameters calculated from the results of the field measurements and laboratory analyses will be reviewed to ensure that all data are scientifically valid, of known and documented quality, and where appropriate, legally defensible. In addition, the performance of the overall measurement system will be evaluated in terms of the completeness of the project plans, effectiveness of field measurement and data collection procedures, and relevance of laboratory analytical methods used to generate data as planned. Findings of the data quality assessment, in terms of data usability, are presented in the annual and five-year project reports.

Components of a data quality assessment include:

- summary of the problems, data generation trends, general conditions of the data, and reasons for data qualification as presented in the laboratory data narrative,

- evaluation of QC information, such as field and laboratory duplicates, blanks, the field staff duplication run, and calibration logbooks, to assess the quality of the field activities and laboratory procedures
- assessment of the quality of data measured and generated in terms of accuracy, precision, and completeness,
- summary of data usability. Sample results for each analytical method are qualified as acceptable, rejected, estimated, biased high, or biased low.

### **C1.3 Field Readiness Review**

The field readiness review is a systematic, documented review of the readiness for the startup of the field effort described in this QAPP. Prior to the start of each year's monitoring effort (winter), IDEQ and Tribe staff will review and comment on each other's field readiness in terms of instrumentation, equipment, and supplies, along with establishing an agreed upon sampling schedule for the upcoming year.

## **C2 REPORTS TO MANAGMENT**

After each sampling visit, once the field collected data have been entered electronically, IDEQ and the Tribe will exchange Excel spreadsheets of the collected field data. After each sampling visit a laboratory data report is received with sample station results and results of all specified QC measures listed in Section B5. Copies of the laboratory reports are exchanged between IDEQ and the Tribe, and there will be communication of any detected problems within the QC results. A step toward corrective actions would include consultations among IDEQ and the Tribe, along with the laboratory QA manager.

IDEQ and the Tribe will prepare field and laboratory data to be submitted once a year to STORET via WQX. Submittal to STORET shall be during the process of preparing annual summary reports, where data quality assessments are finalized for the year, and judgments are made on the usability of data for submittal to STORET.

### **C2.1 Annual Data**

IDEQ and the Tribe will separately prepare annual data summary reports. The annual reports shall be prepared during the winter following each field season and completed by March or April in the following year. The annual reports shall be sent to the distribution list of section A3 and shall be made available to any person or agency upon request.

Annual reports will include an Appendix, where similar to the USGS Water Resources Data reports, there will be tables of all field collected data and laboratory data. Analysis and data presentation in the yearly reports will generally be limited to box plots, tables of computed central tendency, and/or profile graphs. Interpretation and evaluation will generally be limited to identification of any potential significant anomalies or concerns that may require early attention (e.g. pointing to immediate actions needed within the realm of the LMP), before consideration in the more comprehensive 5-year reports. Data generated from the BEMP program will likely be included with the annual summary analysis. The reports may also include discussion of

ELCOM-CAEDYM model run results. A data quality assessment (section C.1.1) will be included that documents and discusses QC results, data usability, and corrective actions.

The annual reports will also offer the opportunity to examine the work plan specifics of the monitoring program. There may be adjustments recommended in the way schedules, sites, and parameters are sampled. Data trends may point to additional sampling points such as in shallow bays or even tributaries which are suspected to be high nutrient loaders.

## **C2.2 Five-Year Data Analysis and Assessment Reports**

The Coeur d'Alene Lake Monitoring Program assumes that extensive analysis of accumulated monitoring data (going back to the baseline study of 1991-92) will be conducted at five-year intervals to support and coincide with a five-year review, which will update and recommended changes to the lake management plan. The five-year data analysis and assessment report will be jointly prepared by IDEQ and the Tribe, and the initial five-year report will be published during the spring of 2016.

The five-year report will be a comprehensive examination of water quality trends over time and geographically from southern to northern waters. It will incorporate data collected by other programs including BEMP and lake research that may be funded and conducted over the next five years. The analysis will examine land use patterns and events such as continued growth and development around the shoreline of Coeur d'Alene Lake and CERCLA remedial projects upstream of the lake. There will be analysis of model scenarios from the ELCOM-CAEDYM model. In particular, the five-year analysis will examine if there are declining trends in water quality such as increases in nutrient concentrations, primary productivity, or metal flux from lakebed sediments, and declining dissolved oxygen levels in the hypolimnion. If such trends are detected, there will be examination of data which may point to the source and cause of water quality degradation.

The LMP, and this monitoring program which is meant to assist in LMP decisions and implementation actions, is considered an adaptive management approach. Both the LMP and monitoring program are expected to evolve to reflect a better understanding of basin and lake processes and incorporate needed modifications in LMP implementation efforts and monitoring tools and techniques.

## **C3 NONCONFORMANCE AND CORRECTIVE ACTION**

This QAPP, the lake monitoring work plan which is incorporated in the QAPP, and SOPs of participating agencies and laboratories, establish the baseline for assessing the quality system. Management and technical staff will follow these plans and procedures during the course of all project activities. However, nonconformances do occur, and each will be documented in a separate QA/QC project notebook by personnel observing the nonconformance. Notebook entries will provide the details of a nonconformance, date of observation, staff name making the entry, and later, any corrective action taken (see paragraph below). Examples of nonconforming work include the following:

- Data falling outside established DQO criteria

- Sample contamination
- Sample chain-of-custody documentation missing or deficient
- Measurement equipment failure including calibration failure
- Unapproved or unwarranted deviations from established procedures, including electronic data entry
- Unforeseen or unplanned circumstances that result in services that do not meet quality/technical requirements

Results of QA reviews and audits typically identify the requirements for a corrective action. The IDEQ and Tribe program managers, along with the laboratory QA manager, are responsible for reviewing all audit and nonconformance reports to determine areas of poor quality or failure to adhere to established procedures. The program managers determine the root cause of poor quality or failure and execute the corrective action as developed and scheduled. Corrective action measures will be selected to prevent or reduce the likelihood of future occurrences and to address the root causes to the extent identifiable.

Where program managers identify or label occurrences of “significant nonconformance”, and the program managers develop and schedule a corrective action, EPA advises that description of the nonconformance and recommended corrective action be examined by an independent reviewer prior to carrying out the action. The independent reviewer is a person not involved in the day-to-day operations of a project and thus avoids a possible bias by project personnel. For IDEQ, the independent review and concurrence for a report of significant nonconformance and corrective action will be done by staff in the State Quality Assurance Program in Boise, Quality Assurance Program. In the event of “significant nonconformance” requiring implementation of corrective actions, the Tribe’s program manager will consult with other technical staff having experience in water quality monitoring from other Tribal natural resource management program areas such as fisheries, water resources and lake management, and if absolutely necessary, consult with limnological experts with whom it has developed a trusted professional relationship and worked with in the past.

## **PART D. DATA VALIDATION AND USABILITY**

### **D1 DATA REVIEW, VALIDATION AND VERIFICATION REQUIREMENTS**

This section describes data review, which is the process of technically reviewing analytical data using written data validation protocols and qualifying measurement results using data qualifiers. The primary objective of data review is to determine if project data are of sufficient quality to support the project objectives. After the data review process is completed, data qualifiers are appended to measurement values by the data reviewer. Final usability of qualified data will be determined by the IDEQ and Tribe project team.

### **D2 VALIDATION AND VERIFICATION METHODS**

Data review is done on a continual and consistent basis during the conduct of the monitoring program. Data review of field measurements begins with pre-visit calibration at the office-lab. If for example, calibration procedures fail with the Hydrolab<sup>®</sup> DS5 multiprobe, and cannot be rectified, it is the responsibility of the technician to deem that the equipment is unsuitable for collecting correct information in the field the next day. In the field, experienced staff can determine when instrument operation is malfunctioning or giving false readings (for example, highly deviant or unusual readings for temperature, pH, or dissolved oxygen). Section B10 describes data entry validation procedures that will be used for entering project field and laboratory data into Excel spreadsheets.

Section B5 describes data quality review performed by IDEQ and Tribe program managers based on method performance criteria and QC criteria documented in the QAPP. From laboratory data reports, program managers review hold times, field duplicates and blanks, laboratory duplicates and blanks, matrix spike/matrix spike duplicate recoveries, and reporting limits. There is an assessment of incidences of poor QC results. Program managers confer, along with communication with the laboratory QA manager, to determine the cause of poor results and then plot out a course of corrective action.

Program managers will confer to assign data qualifications (flags) when required, such as labeling outliers, rejecting data as unusable or unreliable, or assigning estimated values to measurement values below the laboratory reporting limit.

### **D3 RECONCILIATION WITH DATA QUALITY OBJECTIVES**

Following the data review process, validated data will be assessed by the project managers to determine if the data meet the project objectives. Information from the validation and verification procedures are included in the data quality assessments (section C.1.1) which are documented in the annual project reports.



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**APPENDIX A:  
FIELD FORMS FOR PHYSICAL MEASUREMENT DATA**

**Coeur d'Alene Lake Monitoring Program - LiCor Light Profile Sheet &  
 Environmental Conditions**

**Station:** \_\_\_\_\_

**Date:** \_\_\_\_\_

**Time:** \_\_\_\_\_

**Field Staff:** Glen Rothrock, Glen Pettit, Becki Witherow, Jake Watkins

**Secchi depth wo/tube (m):** \_\_\_\_\_

**Secchi depth with/tube (m):** \_\_\_\_\_

**Secchi depth taken by:** Glen Rothrock, Glen Pettit, Becki Witherow, other

**Photic Zone Depth (m):** \_\_\_\_\_

Water Depth (meters)	LI-193SA underwater sensor Channel 1 $\mu\text{mol s}^{-1} \text{m}^{-2}$	LI190A on-deck sensor Channel 2 $\mu\text{mol s}^{-1} \text{m}^{-2}$	Channel1/ Channel2 percent	Weather Conditions day of sampling	Environmental Conditions day of sampling
1				Sunny	<b>Air Quality</b>
2				Mostly sunny	Forest fires
3				Partly sunny	Field burning
4				Cloudy	Dust storm
5				Mostly cloudy	Pollen
6				Partly cloudy	
7				Overcast	
8				Raining	<b>Lake Pool level</b>
9				Rain showers	Flood condition
10				Light rain	Low pool condition
11				Heavy rain	Summer pool
12				Drizzle	
13				Foggy	<b>Water Surface:</b>
14					White caps
15				Snowing	Large chop
16				Snow showers	Choppy
17				Light snow	Small chop
18				Heavy snow	Ripples
19					Flat
20				Hot	Boat chop
21				Mild	Ice
22				Cold	
23				Windy	
24				Breezy	
25				Calm	

**Comments:** \_\_\_\_\_

### Coeur d'Alene Lake Monitoring Program - Hydrolab Profile Sheet (page 1 of 2)

**Station:** C1 - Tubbs Hill      **Date:** \_\_\_\_\_      **Time:** \_\_\_\_\_

**Field Staff:** Glen Rothrock, Glen Pettit, Becki Witherow, & Jake Watkins

**USGS Site Lat/Long**    47° 39' 00"    116° 45' 30"

**Starting Lat/Long:**    47° \_\_\_\_\_ ' \_\_\_\_\_ "    116° \_\_\_\_\_ ' \_\_\_\_\_ "      **Off point (ft)**

**Ending Lat/Long:**    47° \_\_\_\_\_ ' \_\_\_\_\_ "    116° \_\_\_\_\_ ' \_\_\_\_\_ "      **Off point (ft)**

**Station Depth sonar (m):** \_\_\_\_\_      **Station Depth Hydrolab (m):** \_\_\_\_\_

Hydrolab Depth (meters)	Temp. (C)	DO (mg/L)	% DO Sat.	pH	EC	Chloro. a units	Chloro a volts	Turbidity NTU
0.5								
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								

**Comments:** \_\_\_\_\_

**Coeur d'Alene Lake Monitoring Program - Hydrolab Profile Sheet (page 2 of 2)**

**Station:** C1 - Tubbs Hill      **Date:** \_\_\_\_\_      **Time:** \_\_\_\_\_

Hydrolab Depth (meters)	Temp. (C)	DO (mg/L)	% DO Sat.	pH	EC	Chloro. a units	Chloro. a volts	Turbidity NTU
26								
27								
28								
29								
30								
31								
32								
33								
34								
35								
36								
37								
38								
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## **APPENDIX B: WATER SAMPLING PROCEDURES**

## **I. Pre-Visit Preparation (Office Lab)**

- a) The following equipment will go through the initial cleaning procedure: 1) 2.2 L & 6.2 L non-metallic Kemmerer sample bottles 2) 14 L churn splitter, 3) 6 inch pieces of Tygon tubing attached to capsule filter fittings (two tubing-fittings per filter), 4) a 1000 mL Nalgene filter base with snap-on plastic cap (to receive 0.45  $\mu\text{m}$  filtered water), 5) 500 mL graduated cylinder and 1000 mL filter base – 47 mm holder - 500 mL funnel for chlorophyll *a* samples, and 6) during winter and spring sampling runs, a 1000 mL Nalgene filter base – 47 mm holder - 500 mL funnel with screw-on cap for post-filtering with a 0.2  $\mu\text{m}$  membrane filter.
- b) Following USGS - TWRI methods, Chapter A3, the cleaning procedure is (with personnel wearing powder-free vinyl gloves):
  1. detergent wash
  2. tap water rinse
  3. 5% HCl soak & rinse (the equipment for chlorophyll *a* samples, number 5 above, do not get acid rinsed)
  4. deionized water (DIW) rinse (tubing - fitting sets begin with the acid soak).

Wash each individual part of the filter systems (inside of base including ports, caps, holder, and funnel). Let each piece of equipment air-dry. Reassemble the filter base for chlorophyll *a* and place it in a new plastic bag. Place the Kemmerer bottles and churn splitter into new plastic bags and seal for transport and use in the field. Place the Tygon tubing – fitting sets into two new Ziploc bags (double bagged).

- c) IDEQ and the Tribe prepare the capsule filters and subsample bottles in the field (Step V.1.e.i and V.1.e.ii). On the boat, all subsample bottles are filled to about one-fifth volume with DIW (with field personnel wearing powder-free vinyl gloves). The bottles are shaken vigorously (with caps on) to completely wet and rinse the entire inside surface, and then the DIW is discarded. Repeat a second time. Capsule filters are prepared by running DIW through the filter and attached Tygon tubes with fittings.

## **II. Arrive at a Sampling Station**

- a) Anchor on station (using GPS waypoint). Note depth reading on boat depth sounder.
- b) Record field observations on field forms (time, date, general description of weather – sunshine / cloud cover, wind strength / direction, lake surface conditions – calm, height of waves, any other pertinent info such as water clarity, color, turbidity, etc.)

## **III. Secchi Disk Transparency and Photosynthetically Active Radiation (PAR)**

- a) Determine Secchi disk transparency depth without and with the aid of an aquatic view scope (from shady side of boat, estimate to the nearest 0.1 meter increment). Depth and observing staff member recorded on field.
- b) Set up the Li-Cor<sup>®</sup> instrumentation to measure and record PAR. Place the 190SA deck sensor to receive unimpeded light (representing light incident on the water surface). For

the Tribe, the 193SA underwater spherical sensor is incorporated onto the Hydrolab<sup>®</sup> multiprobe. Light attenuation of PAR through the water column will be recorded with the other Hydrolab<sup>®</sup> profile parameters (Step IV below). As the 193SA sensor is lowered through the water column, determine and record the depth of 1% incident PAR (1% of the light incident at the surface which will define lower limit of photic zone). Determine 1% PAR to the nearest 0.25 m. An additional reading is recorded 1 m below the 1% PAR to determine the extinction coefficient.

For IDEQ the 193SA is not incorporated onto the Hydrolab<sup>®</sup>, it is lowered down the water column with a separate frame and signal cable. Profile PAR down the water column until the 1% incident PAR depth is determined (nearest 0.25 m). Record profile information on a field form. For comparison purposes, record PAR at the Secchi disc depth (with view tube).

#### IV. Water Column Profile - Physical / Chemical Conditions

With submersible instrumentation package (Hydrolab<sup>®</sup>), determine water column physical/chemical data profile: temperature, dissolved oxygen (DO) concentration/saturation, pH, specific conductance, PAR (Tribe only, see above), turbidity and *in-situ* algal chlorophyll *a* fluorescence. Readings will be recorded in the instrumentation software. Readings also will be recorded manually in the trip field notebook to the appropriate decimal precision:

Temperature	nearest tenth of a degree Celsius (°C)
DO concentration	nearest tenth of a milligram per liter (mg/L)
DO % saturation	nearest tenth of a percent
pH	nearest tenth of a standard pH unit
Specific Conductance	nearest whole number of microsiemens per centimeter (µS/cm)
PAR	nearest whole number of micromoles of photons per second per square meter (µmol photons/sec/m <sup>2</sup> ), which is the same as micro-Einsteins per second per square meter, (µE/sec/m <sup>2</sup> )
<i>in-situ</i> algal fluorescence	nearest thousandth of a volt (V) and nearest tenth of a milligram per liter (mg/L)
turbidity	nearest tenth of a nephelometric turbidity unit (NTU)

- a) Collect measurements at 0.5 meters depth (lake surface just covering top of Hydrolab instrument sonde), at 1 m depth, and at 1 - 2 m depth increments down through the thermocline (metalimnion). The thermocline is defined as the zone where water temperature changes 1 degree Celsius (or more) per meter change in depth; particular attention should be given to defining the depth of this zone, if possible, in 0.5 to 1.0 m increments. (NOTE: Extended periods of sub-freezing air temperature or ice cover over

the lake surface can produce “inverse stratification” where near-surface water temperatures approach 0 degrees Celsius and increase with depth to 4 -6 degrees Celsius; particular attention should also be given to defining these conditions throughout the water column when encountered).

- b) During summer months, a zone of maximum phytoplankton density (as indicated by maximum *in situ* chlorophyll *a* fluorescence and subsequent laboratory chlorophyll analyses) is likely to be encountered in the region of the metalimnion, which lies between the warm, sunlit, near-surface epilimnion and the cold, dark, bottom waters known as the hypolimnion. This zone of peak chlorophyll *a* was observed by USGS researchers during a 2004 - 2006 cooperative Coeur d'Alene Lake study with the Tribe. Note and record in the field notebook the depth of maximum chlorophyll *a* fluorescence.
- c) The lower extent of the euphotic zone is defined as the water depth to which 1 percent of the photosynthetically active radiation at the surface penetrates. This also frequently occurs in the region of the thermocline or just below; note the depth (to the nearest 0.25 m), and record in the field notebook.
- d) Continue taking readings at 1 - 2 m increments to about 5 meters below the thermocline; below that (or under conditions of near surface-to-bottom homothermy) readings can be taken at 3 to 10 m increments to 1 m above the bottom. If possible, (e.g. calm surface conditions), gently lower the instrument sonde to the lake bottom (without embedding deeply in bottom sediments and fouling instrument sensors), note the maximum depth displayed (to the 0.1 m increment and record in the field notebook), then raise to approximately 0.2 m above lake bottom, record that depth, and then record the water quality physical / chemical values.

## V. Water Sample Collection and Processing

Depth integrated and discrete water samples will be collected at specific depths with non-metallic Kemmerer or Van Dorn samplers suspended from a stretch-free, depth-calibrated line and closed at a specific depth by a messenger slid down the line. To ensure an adequate amount of water, a sample from a specific depth may be collected more than once and composited in a churn splitter.

### 1. Euphotic Zone Composite Sample Collection

#### a) Sample Bottle Labels

Label all sample bottles with an indelible marker: site name/ID#, date, time, constituents for analysis, and preservative used.

#### b) Field Rinsing the Churn Splitter and Kemmerer

Prior to collecting the 5 sample composite from the euphotic zone, collect a sampler full of lake water from below the water surface (~ 1 m deep) and empty into churn splitter.

Shake vigorously, rinsing the interior surfaces (including the lid) thoroughly and releasing some of contents through the spigot. Empty completely. Repeat once more. IDEQ immerses the churn splitter below the water surface (~ 0.25 m deep), rinses, and then collects a near-full bucket of water. Shake vigorously, rinsing the interior surfaces (including the lid) thoroughly and releasing some of contents through the spigot. Empty completely. Repeat twice. Immerse Kemmerer sampler below the water surface (~ 0.25 m deep) three times.

c) Euphotic Zone Composite Sample Collection

Note the depth at which 1% of the surface PAR occurs; this is the lower depth limit of the euphotic zone (EZ) sample. Using the sampling chart prepared for equal depth samples at 0.25 m resolution, collect 5 equally spaced discrete samples with the sampler, from 1 m depth to the 1% incident PAR depth. NOTE: the sampler suspension line should be non-stretching, with the “zero” point set at the mid-point of the sampler body when hanging vertically, and calibrated (marked) accordingly in 0.25 m increments.

**Example:**

EZ depth (depth at which 1% of incident surface solar radiation occurs) = 17.5 m.  
Samples are collected at: 1.00 m, 5.25 m, 9.25 m, 13.50 m, and 17.50 m.

While wearing powder-free vinyl gloves, composite the samples by carefully emptying sampler contents into the churn splitter through the sampler spigots or by carefully opening the lower end seal and letting the contents drain directly into the churn without spilling. Care must be taken to ensure sample does not contact gloved hands or other potentially contaminating surfaces and no water drips from the line which has been in contact with deck bilge.

(NOTE: USGS researchers used a 3-point euphotic zone composite in the 1990 - 1994 lake studies. In the 2004 - 2006 studies USGS used a continuous pumping sampling method through the euphotic zone. In the monitoring discussed here, a 5-point euphotic zone composite will be collected to more closely duplicate the continuous pumping method using 2.2 L samplers and a 14 L churn splitter so that 5 sampler volumes can be fit into a single churn splitter.)

d) Collect Samples for Chlorophyll *a*, Phytoplankton, Total Metals and Total Nutrients

For water chemistry constituents/parameters requiring unfiltered samples (or for samples that will be collected by a subsequent filtration process such as chlorophyll *a*), subsamples for laboratory analysis will be withdrawn directly into appropriate sample containers from the well-mixed contents of the churn splitter; these subsamples will be withdrawn from the churn splitter first.

i) *Phytoplankton Subsample*

From the euphotic zone composite sample in the churn splitter, withdraw (while churning) a subsample into a 125 mL brown plastic bottle. Add 1.5 mL Lugols iodine solution. Cap and invert several times to mix. Label appropriately.

ii) *Chlorophyll a Subsample*

From the euphotic zone composite sample in the churn splitter, partially fill (while churning) a 500 mL graduated cylinder, shake, and dispose of the sample as a field rinse. Fill the graduated cylinder again for subsequent filtration of chlorophyll *a* sample onto a glass-fiber filter.

Assemble the vacuum pump, filter plate with glass fiber filter with rough side up (Advantec MFS GF-75, 0.3  $\mu\text{m}$  nominal rating 47 mm diameter), and receiver/funnel filtration apparatus.

Working in the shade and out of direct sunlight, slowly filter 500 mL of water in the graduated cylinder through the glass-fiber filter. Vacuum should be kept to less than 5 inches Hg and the graduated cylinder holding the sample should be swirled occasionally to keep the algal cells in suspension. Refill the 500 mL graduated cylinder once more and process just like the first 500 mL. Rinse down the sides of the graduated cylinder with DIW after the last of the sample is poured into the filter funnel, swirl again and pour into funnel. When the last of the sample in the filter funnel is about 1 cm deep, add 3 drops of  $\text{MgCO}_3$  buffer solution. Gently rinse down sides of funnel with DIW to entrain all algal cells present on filter.

Release vacuum, remove filter from plate with forceps, and place in plastic Petri dish. Label the Petri dish with sample number, station ID, date/time, and volume filtered. Wrap the Petri dish in foil, label outside of foil, and place in small zip-lock bag. Immediately place on dry ice in a separate small cooler. Immediately place in freezer upon return from sampling. Keep frozen at all times during shipment to lab for analysis. Ship overnight express in cooler with dry ice.

iii) *Total Nutrients and Metals*

With field sampling personnel wearing powder-free vinyl gloves (changed out with each sample set processed), all subsample containers will be rinsed twice with native sample water from the churn splinter (except for IDEQ total nitrogen glass vials which are pre-loaded with HCl and are not to be pre-rinsed). From the spigot, pour about a one-fifth bottle volume into the bottle, shake vigorously to completely wet and rinse the entire inside surface (with cap on), discard water, repeat once more.

While churning, fill subsample bottles for total metals, total phosphorus, and total nitrogen. Leave enough space for preservative acids (not needed for IDEQ total nitrogen vials). Cap bottles.

Add appropriate volume of sulfuric acid preservative to the total nutrient samples (except for IDEQ total nitrogen vials). Add sulfuric acid prior to adding nitric acid preservative to metal samples in order to minimize potential for contamination of nitrogen series samples. Add appropriate volume of nitric acid preservative to the total metals (and hardness) sample bottle. Put a check mark on the bottle caps representing that the sample is fixed.

Preservative acids are to be certified ultra-pure, source/supplier specified and/or supplied by the labs. Appropriate acid preservative volume depends on sample bottle size and acid concentration. Acid is added to lower the pH of the sample water to <2 pH. For concentrated sulfuric and nitric acids, the volume rate is 2 ml acid per 1 L of sample water.

Empty preservative acid vials should be placed in a 1 L bottle filled with approximately 500 mL of water; agitate occasionally so that empty vials become filled with water to dilute residual acids. The bottle and lid should be clearly marked so that it is not inadvertently used on actual sample bottles. Dispose of as household garbage at the end of the day.

Put sample bottles in Ziploc bags labeled for each sample depth zone. To minimize the potential for contamination, samples preserved with nitric acid (trace-metals samples) should not be placed in bags with nutrient samples (unpreserved or preserved with sulfuric acid). Place total nutrient samples in an ice chest with sufficient ice to keep the temperature at 4 °C or less. Generally, it is not necessary to chill the trace-metals samples, however, they should not be left in the open exposed to direct sun and heat for extended time periods. Place total metals in a separate container.

e) Collect Samples for Dissolved (Filtered) Nutrients and Metals

The Tribe and IDEQ have different procedures for processing filtered samples because the Tribe uses a battery powered peristaltic pump for forcing water through the 0.45 µm capsule filters, while IDEQ uses a battery powered vacuum bell-aspirator to pull water through the filter. Procedures for DIW rinsing of filters, collection of filtered native rinse water, and collection of filtered sample water are described separately.

i) *IDEQ DIW Rinse of Capsule Filters*

Subsample bottles for filtered samples are first rinsed with DIW as previously described in Step I.d. For capsule filter rinses, place a 10 L carboy of DIW on the boat work bench. Retrieve 2, Tygon tubing – fittings and remove a capsule filter from the sealed, shipping plastic bag. Attach a Tygon tubing – fitting apparatus at each end of the capsule filter.

Attach the inlet flow end of the Tygon tube to the spigot of the 10 L carboy (capsule flow-arrow away from carboy). Place outlet end of tubing pointing up at an acute angle from the horizontal plane (expels trapped air), and turn spigot on.

Allow water to flow through filter freely before connecting to filter base. Attach the outflow Tygon tube to a Nalgene filter base port. Attach Tygon tube of the 12 volt, bell-aspirator (vacuum pump) to the other filter base port. Turn on aspirator, and set pressure at no greater than 8 inches Hg (at times, DIW flows freely enough through the capsule filter such that the aspirator is not needed).

Draw about 1 liter of DIW through the capsule filter into the filter base. Turn off vacuum, and turn off carboy spigot. Remove tubing from DIW carboy, hold inlet end of tubing up, and operate vacuum pump to drain as much as possible of the DIW that remains in the filter unit. While the pump is operating, shake the capsule filter to help remove any entrained DIW. Do not cover the open end of tubing while drawing DIW from filter. Turn pump off, disconnect from filter base port, and discard water in filter base.

ii) *Tribe DIW Rinse of Capsule Filters*

Samples will be filtered under positive pressure provided by a battery-powered, adjustable-speed peristaltic pump and using disposable 0.45 µm pore-size capsule filters generally following the procedures developed by USGS and used by researchers in the 2004 – 2006 Coeur d'Alene Lake studies. Wearing a new pair of powder-free vinyl gloves, punch inlet and outlet ends of the capsule filter through bag (leave bag on the filter), attach filter inlet to peristaltic pump outlet hose. (NOTE: flow through filter is directional – make sure flow direction is correct as indicated by arrow on filter). Pump 1 L of DIW through filter, holding the filter outlet upright (to fill filter completely leaving no “bubbles” or dry spots throughout filter media). Use a small bucket to collect all rinse water from filter preparation/decontamination and bottle rinsing steps. Continue pumping to clear all DIW rinse water from lines. With the filter outlet pointing down, shake out excess water. Clamp filter into stand with filter outlet pointing down.

iii) *IDEQ Collection of Filtered Samples*

Attach the inlet Tygon tube to the spigot of the churn-splitter. Place outlet end of tubing pointing up at an acute angle from the horizontal plane (expels trapped air), and turn spigot on. Allow water to flow through filter freely before connecting to filter base. Attach outlet end to the Nalgene filter base port. Attach the vacuum pump to the other filter base port.

Turn on vacuum pump and set pressure at no more than 8 inches Hg. Draw about 800 mL of sample water through the capsule filter into the filter base (for a native water rinse of filtered water). During the process to collect filtered water, circulate the water in the churn splitter by moving the handle up and down slowly. Turn off vacuum, detach outlet tube of filter from the filter base, clamp outlet hose with a tubing clamp, leave spigot on.

Field rinse the five sample bottles for dissolved constituents: dissolved metals

(500 mL), dissolved nitrate (500 mL), dissolved ortho-phosphate (250 mL), total dissolved phosphorus (250 mL), and dissolved ammonia (50 mL). For each sample bottle, place about one-fifth bottle volume of filtered water into the bottle, cap, shake vigorously, and discard water. Repeat once more for each bottle. Discard remaining water in filter base.

Reattach capsule filter tubing, undo clamp, and begin vacuum pump. Collect at least 1000 mL of filtered water. During the process to collect filtered water, circulate the water in the churn splitter by moving the handle up and down slowly. Turn off vacuum, detach outlet tube of filter from the filter base, clamp outlet hose with a tubing clamp, and leave spigot on. While leaving enough space for preservative acids, pour about 500 mL of the filtered sample into the sample bottle labeled for dissolved metals. Pour the remaining 500 mL into the sample bottle for dissolved nitrate. Reattach capsule filter tubing, undo clamp, and begin vacuum pump. Collect at least 500 mL of filtered water. Pour 250 mL of water into the sample bottle for total dissolved phosphorus. Pour the remaining 250 mL of filtered water into the sample bottle for dissolved ortho-phosphate, or pour 50 mL of filtered water into the sample bottle for dissolved ammonia. If needed, collect at least an additional 50 mL of filtered water, and pour it into the 50 mL centrifuge tube for dissolved ammonia.

Discard filter capsule, and place Tygon tubing – fittings into Ziploc bag for future office 5% HCl soak, DIW rinse, and future field reuse.

iv) *Tribe Collection of Filtered Samples*

Place pump inlet hose into churn splitter, ensuring that hose end will remain submerged through entire pumping procedure. Care should be taken to minimize hose contamination (especially the inlet hose which is placed into the churn splitter) by thorough rinsing of the outside with DI water, minimizing contact with potentially contaminating surfaces, handling only with gloved hands, and storing/transporting while coiled in a zip-lock bag.

Switch on pump. After the filter fills and a stable and steady stream of water is emerging from filter outlet (e.g. no bubbles or pulsations other than those from the action of the pump itself), the triple-rinse (native filtered water) of sample bottles and collection of the filtered samples can begin. The pump can be switched off between rinses and filling of different bottles. The goal is to pump as little water through the filter as necessary while adequately rinsing and filling bottles to minimize loading of the filter media with particulate matter, thus maintaining as near constant as possible filtration conditions and filtrate characteristics during the collection of the several filtered subsamples. While filling bottles for the samples, leave enough space for preservative acids. Cap bottles.

v) *Preservation of Filtered Samples, IDEQ and Tribe*

Add appropriate volume of sulfuric acid preservative to the total dissolved phosphorus, dissolved nitrite and dissolved nitrate, and dissolved ammonia sample bottles. Add sulfuric acid prior to adding nitric acid preservative to metal samples in order to minimize potential for contamination of nitrogen series samples. Add appropriate volume of nitric acid preservative to the dissolved metals (including dissolved calcium and magnesium) sample bottle. Put a check mark on the bottle caps representing that the sample is fixed. The sample for dissolved ortho-phosphate **does not** receive acid preservative.

Place dissolved nutrient samples in the same Ziploc bag as total nutrients. Place back in ice chest. Place dissolved metals sample in container with total metals. Assure that all bottles are properly labeled.

Assure that all information has been recorded that will be required for lab analysis request / chain-of-custody forms.

vi) *Collection of Filtered Samples Through a 0.2 µm or 0.1 µm Filter*

During lake conditions of high turbidity, there have been occasions where water filtered through the 0.45 µm capsule filters exhibit noticeable fine particulate matter. According to the EPA lab SOP, if a shaken filtered sample has a turbidity of >1 NTU, the filtered sample is acid-digested and then analyzed. This releases metals adsorbed to the fine colloids and produces a high bias for some of the dissolved metal concentrations. Furthermore, there is evidence that suggests that metals-enriched colloids may be suspended in the water column during other periods of the year and may not be visible to the naked eye. Given the potential presence of colloids and their ability to pass through a 0.45 µm filter, IDEQ and the Tribe have decided that on sampling occasions where there are visible floating particulates, both agencies will post-filter water that has passed through the 0.45 µm capsule filters through an additional filter process. IDEQ will also collect post-filtered samples throughout the year to determine the fraction of metals passing through the 0.45 µm capsule filter.

After collecting all of the filtered samples described in Steps *iii* and *iv* above, collect another 1000 mL of filtered water through the 0.45 µm capsule filter. Cap the Nalgene filter base and set aside. Discard filter capsule, and place Tygon tubing – fittings into Ziploc bag.

*Tribe Procedure:*

Retrieve the Nalgene filter base – 47 mm holder - 500 mL funnel with screw-on cap for post-filtering with a 0.2 µm membrane filter. Using forceps, carefully place a 0.2 µm membrane filter onto the grated holder of the filter base. Attach the 500 mL funnel, attach a vacuum pump, place about 250 mL of 0.45 µm filtered water into the funnel for a native rinse, and attach screw-on cap (leave one port open on the cap). Turn on vacuum pump and set pressure no higher than 8 inches Hg. Filter the 250 mL (may take up to 15 minutes, filtering is very slow for the 0.2 µm filter). **Turn off vacuum pump, wait a few seconds, and release pressure by**

**slowly unscrewing the funnel. Excess vacuum pressure must be relieved slowly or membrane filter will rupture.** Field rinse 3 times, the 500 mL sample bottle for 0.2 µm dissolved metals. Discard remaining water in filter base.

With the 0.2 µm filter still in place, reattach the 500 mL funnel. Place 500 mL of 0.45 µm filtered water into the funnel and attach cap. Filter. Pour 500 mL of the filtered sample into the sample bottle labeled 0.2 µm filtered for dissolved metals. Fix/preserve the sample with the appropriate volume of nitric acid. Cap, label, and put a check mark on the lid representing that the sample is fixed. Place in container with other metal samples. Conduct a 5% HCl rinse - DIW rinse of the filter base and funnel. Place in Ziploc bag.

*IDEQ Procedure:*

In 2011 IDEQ started using Millipore Express® PLUS 0.1 µm Stericup disposable, single use membrane filters. In the field, after collecting 0.45 µm filtered water, remove Stericup® from sterile package. Attach the Stericup® to a vacuum pump. Place 250 mL of DIW into the funnel and attach cap. Turn on vacuum pump, and set pressure to no higher than 8 inches Hg. Disconnect the vacuum pump, discard the filtered DIW, and re-attach the Stericup to the vacuum pump. Filter 250 mL of 0.45 µm filtered water through the funnel twice for a native rinse, discarding the rinseate after each filtration. Place 250 mL of 0.45 µm filtered water into the funnel and attach cap. Filter. Pour 250 mL of the filtered sample into the sample bottle labeled “0.1 µm filtered for dissolved metals.” Repeat once more to obtain 500 mL. Fix/preserve the sample with the appropriate volume of nitric acid. Cap, label, and put a check mark on the lid representing that the sample is fixed. Place in container with other metal samples. Discard disposable Stericup.

## **2. Discrete Sample Collection below the Photic Zone**

### a) Field Rinsing the Churn Splitter & Kemmerer Samplers

Between each sampling zone at a particular sampling site, conduct a DIW rinse of the 2.2/6.2 L Kemmerer bottle, 14 L churn splitter, and 1000 mL Nalgene filter base with plastic cap prior to sampling the next depth zone. Prior to moving to the next sampling site, or at the end of a sampling day, conduct a 5% HCL rinse followed by a DIW rinse of the 2.2/6.2 L Kemmerer bottle, 14 L churn splitter, and 1000 mL Nalgene filter base with cap. Do these procedures while wearing gloves.

For Tribe decontamination between sample depths and transport, follow these procedures: 1) while still wearing gloves, remove the capsule filter from the peristaltic pump outlet hose and discard, 2) run pump until hoses are empty, 3) pump 1 L of 5% HCl (prepared from lab-certified contaminant-free concentrate) through hoses, 4) while holding hoses over waste bucket, rinse outside of hoses with deionized water using a spray bottle, and 5) carefully coil hoses into zip lock bag (without removing from pump), seal bag as much as possible.

For samples at the discrete depths (i.e. chlorophyll *a* maximum, 20 m, 30 m, and 1 m off bottom), while wearing gloves, collect a sampler full of water from that depth and place about a one-third volume into the churn splitter. Shake vigorously, rinsing the interior surfaces (including the lid) thoroughly and releasing some of contents through the spigot. Empty completely. Repeat once more with the remaining water in the sampler bottle. IDEQ completely empties the sampler into the churn splitter, shakes vigorously, rinsing the interior surfaces (including the lid) thoroughly and releasing some of contents through the spigot.

b) Collection of Samples at Discrete Depths

Collect water samples from desired depth with Van Dorn/Kemmerer sampler; collect enough sampler volume to fill the churn splitter with enough water for bottle rinsing, withdrawal of appropriate subsample volumes, and sample replicates if scheduled.

Collection of samples 1 m above bottom is determined by the station depth recorded with the Hydrolab and sonar. If any signs of entrained bottom sediment are observed in the sample bottle, discard the sample and clean sampler with 5% HCl solution and DIW. Repeat the process until a clean sample is obtained.

c) Process Samples for Total and Dissolved Nutrients and Metals

Follow the same procedures as described in Steps V.d and V.e above.

**APPENDIX C:**  
**List of Sampling Equipment, Supplies, and Reagents**

## Field Equipment

1. Li-Cor<sup>®</sup> system of LI-1400 DataLogger, deck-side 190SA Quantum Sensor, and a 193SA Underwater Spherical Quantum Sensor (IDEQ). Tribe has 193SA sensor incorporated onto Hydrolab<sup>®</sup> with readings logged into Hydrolab software.
2. Hydrolab<sup>®</sup> DS5 multiprobe (100 m cable) with chlorophyll *a* sensor
3. Handheld GPS units
4. 2.2 & 6.2 L Kemmerer, non-metallic (IDEQ), 2.2 L Von Dorn sampler (Tribe)
5. 14 L Churn Sampler
6. 12 volt vacuum bell-aspirator (IDEQ), peristaltic pump (Tribe)

## Field and Lab Supplies

1. Winch and depth meter for Kemmerer and Von Dorn
2. Non-stretching, high quality woven, 1/4" cord for Kemmerer (60 m length)
3. 20 cm black & white Secchi disk with measuring cord or chain
4. Nalgene 1000 mL filter base with plastic lid, for filtered metals and nutrients (IDEQ)
5. Millipore groundwater filter capsule, 0.45  $\mu\text{m}$  pore size, 600  $\text{cm}^2$  filter area
6. Tygon tubing, 1/4" internal diameter
7. 1000 mL (IDEQ) and 500 ml PreCleaned Certified<sup>™</sup>, HNO<sub>3</sub> rinsed, clear HDPE sample bottles (for metals)
8. 250 mL, clear, HDPE sample bottles from SVL Analytical for nutrients (IDEQ)
9. 500 mL clear, HDPE sample bottles (Tribe and IDEQ)
10. Nalgene 1000 mL filter base – 47 mm holder - 500 mL funnel, for chlorophyll *a*
11. 500 ml graduated cylinder, Teflon, for chlorophyll *a* water
12. Advantec MFS GF-75, 0.3 $\mu\text{m}$  nominal rating pore size, 47 mm diameter glass filter fiber for chlorophyll *a*
13. Double capped Petri dishes, 47 mm diameter
14. Aluminum foil
15. Stainless steel tweezers
16. 125 ml brown HPDE sample bottles for phytoplankton ID
17. 0.2  $\mu\text{m}$  membrane filters (e.g. Nuclepore) for post-filtering of 0.45  $\mu\text{m}$  filtered water
18. Nalgene 1000 mL filter base – 47 mm holder - 500 mL funnel with screw-cap for 0.2  $\mu\text{m}$  filtered water
19. 4 L LDPE jugs for 5% HCl rinse, DIW, and IBW
20. 10 L LDPE carboys with spigots for DIW and IBW
21. 500 mL glass graduated cylinder for preparing 5% HCl acid rinse solution
22. 1.5 mL graduated, disposable polyethylene pipets for MgCO<sub>3</sub> and Lugols
23. Safety wash bottles for 5% HCl rinse solution
24. Wash bottles for DIW and IBW
25. Vinyl, powder free gloves
26. Safety glasses
27. Rubberized cloth apron
28. Nonmetallic bottle brushes and non-colored sponges
29. Field logbooks, water resistant paper
30. Logbook for in-office equipment calibrations and QA/QC notes and actions
31. Coolers, ice packs, and dry ice for sample storage and shipping
32. USEPA COC seals

33. Millipore Express® PLUS 0.1 µm Stericup membrane filters for post-filtering of 0.45 µm filtered water

### Reagents

1. Certified, contaminant-free water (inorganic blank water, IBW)
2. Deionized water (DIW)
3. Phosphate-free detergent (e.g. Liqui-Nox)
4. Hydrochloric acid (HCl), Trace Metal Grade, to prepare 5% solution for cleaning (acid rinses)
5. Nitric acid (HNO<sub>3</sub>), concentrated (70%), in 1 mL ampules or poor vials for preservation of metal samples, certified trace-metal grade
6. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), concentrated (90%), in 1 mL and 0.5 mL ampules or poor vials for preservation of nutrient samples
7. pH 7 & 10 buffer solution to calibrate Hydrolab pH probe
8. Potassium chloride conductivity standard 84 µmhos/cm to calibrate Hydrolab conductivity probe
9. Hach, Winkler DO kit to check calibration on Hydrolab DO probe
10. Lugols solution for phytoplankton ID samples
11. Saturated MgCO<sub>3</sub> solution for chlorophyll *a* filters
12. Turbidity standards 0.0 NTU, 40 NTU and 100 NTU to calibrate Hydrolab



**APPENDIX D:  
LABORATORY CHAIN OF CUSTODY FORMS**