# Quality Assurance Project Plan

## Arsenic Monitoring to Support Human Health Criteria Adoption

**State of Idaho**
**Department of Environmental Quality**

**Water Quality Division**

**Version 1.0**

**August 14, 2019**

# 1 Title and Approval Page

## Quality Assurance Project Plan

**Title**: Arsenic Monitoring to Support Human Health Criteria Adoption

**Region/Division**: Water Quality Division

**Version Number**: 1.0

## Date: August 14, 2019Approval Signatures

Note: This QAPP becomes effective on the date of the last approval signature.

**Project Manager/Author**

Signature: _____ 8/13/2019

Name: Ian Wigger, Water Quality Standards Analyst, Water Quality Div. Date

**Project Quality Assurance Officer**

Signature: Amanda Laib 8/13/2019

Name: Amanda Laib, Water Quality Analyst, Technical Services Div. Date

*Note: At the time of QAPP signature, the project QAO is required to update the DEQ QAO project document tracker, found at EDMS # **2012AEB8**.

**Program or Regional Manager**

Signature: _____ 8/13/2019

Name: Jason Pappani, Surface Water Bureau Chief, Water Quality Div. Date

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# 3 Distribution List

At a minimum, the following personnel and analytical laboratory contacts will receive either an electronic or hard copy of the final signed quality assurance project plan (QAPP) (Table 1).

**Table 1. Project QAPP distribution list.**

| Name | Project Affiliation | Organization and Address/Location | Contact Number |
|---|---|---|---|
| Kiley Mulholland | DEQ Quality Manager | DEQ-Technical Services | (208) 373-0405 |
| Jason Pappani | Program or Regional Manager | DEQ-State Office, Water Quality Division | (208) 373-0119 |
| Amanda Laib | Project Quality Assurance Officer | DEQ-Technical Services | (208) 373-0133 |
| Ian Wigger | Project Manager | DEQ-State Office, Water Quality Division | (208) 373-0147 |
| Hawk Stone | Project Staff | DEQ-Technical Services | (208) 373-0588 |
| Elizabeth Madonick | Analytical Laboratory | Brooks Applied Labs | (206) 632-6206 |

# 4 Project/Task Organization

Key project personnel and their responsibilities are defined in Table 2. An organizational chart is provided in Figure 1.

The project staff duties and responsibilities described in Table 2 are not intended to be all inclusive; see sections 1.2.5 through 1.2.7 of the DEQ *Quality Management Plan* (QMP) (DEQ 2017) for a more detailed description.

**Table 2. Key project personnel and associated responsibilities.**

| Name | Project Title/Responsibility |
|---|---|
| Jason Pappani | **Program or Regional Manager**:<br>• Assists in the review of the QAPP and signs the final QAPP as an approver.<br>• Confirms the project QAPP meets the needs of the program/region.<br>• Ensures the QAPP is approved prior to the start of project work.<br>• Ensures the program/regional procedures and policies referenced in the QAPP are current and approved for use.<br>• Performs all duties and responsibilities as assigned in the project QAPP.<br>• Selects and assigns a project quality assurance officer (QAO), who meets the criteria for independence defined in the DEQ QMP (see QAO duties below). |
| Amanda Laib | **Project Quality Assurance Officer**:<br>• Assists in the review of the QAPP, verifies the QAPP meets the requirements of the DEQ QMP, and signs the QAPP as an approver.<br>• *When the project QAO signs the QAPP for approval, the QAO is required to update the DEQ QAO project document tracker found at the electronic document system (EDMS) # **2012AEB8**.*<br>• Performs an annual audit, using the QAO audit checklist located in Appendix A, on all assigned projects to evaluate project compliance with the approved project QAPP. Files the completed audit checklist in the EDMS to document the audit.<br>• Provides data validation per the project QAPP, using the appropriate checklist located in Appendix A, and may also participate in final project report review.<br>• Documents all audit and data validation activities in the DEQ EDMS<br>• Performs all other duties and responsibilities as assigned in the project QAPP. |
| Ian Wigger | **Project Manager**:<br>• Serves as the primary author of the project QAPP, and signs the final QAPP as an approver.<br>• Performs overall project planning, document development and approval, sample planning and coordination, laboratory coordination, reporting functions, project report/summary development, and project file maintenance in the EDMS.<br>• Ensures each project involving activities not covered in the *General* Safety *Manual* (DEQ 2018a) has an approved health and safety plan (HASP) as required in the *Safety Program Plan* (DEQ 2018b).<br>• Enters the approved and current project QAPP in the EDMS, including a copy of the signed approval page.<br>• Ensures all project work is conducted in accordance with the DEQ QMP, the approved QAPP, and the applicable standard operating procedures.<br>• Ensures personnel assigned to this project are appropriately trained and qualified, with the corresponding training records on file in human resources.<br>• Performs data review and verification per the project QAPP, using the appropriate checklists located in Appendix A.<br>• Reviews the project QAPP/FSP and standard operating procedures (SOPs) annually to determine if revision is necessary<br>• Documents all audit and data review/verification activities in the DEQ EDMS<br>• Performs all other duties and responsibilities as assigned in the project QAPP. |
| Elizabeth Madonick | **Laboratory Contact/Manager**: This person is the primary contact at the laboratory for DEQ project staff |

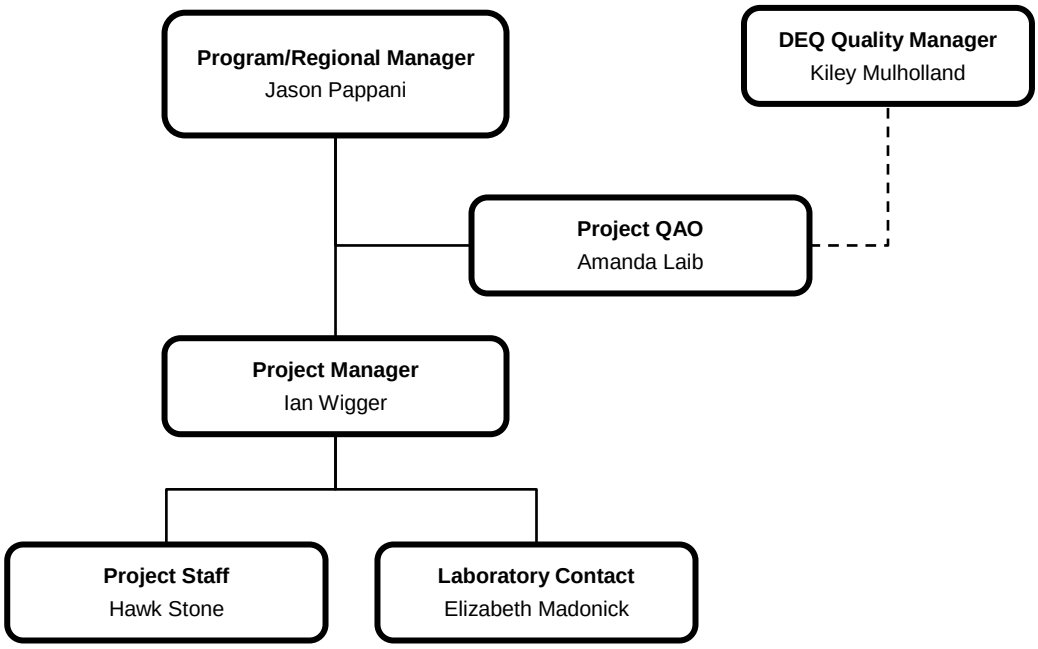


**Figure 1. Project organizational chart.**

# 5 Problem Definition/Background

## 5.1 Problem Statement

EPA recommends two criteria for protection of human health under section 304(a) of the Clean Water Act (CWA). The two criteria are for exposure through fish consumption only and for exposure through both drinking water and the consumption of fish.

The current 304(a) EPA recommended arsenic criteria values are 0.14 fish consumption only and 0.018 µg/L both drinking water and the consumption of fish, were adopted in 1992. This criterion of fresh weight fish is based on protecting a person weighing 70 kilograms (155lbs) who eats on average of 17.5 grams of fish per day—about one 8-ounce meal every other week over their lifetime. The more recent Safe Drinking Water Act (SDWA) Maximum Contaminant Level (MCL) is 10 µg/L.

Idaho adopted 10 µg/L as its CWA arsenic criterion for both exposures in 2008, choosing the SDWA MCL due to concerns about background levels that exceed EPA's 304(a) criteria. In 2010 EPA approved 10 µg/L as its CWA arsenic criterion for both exposures. In June of 2015 Northwest Environmental Advocates challenged EPA's approval 10 µg/L as its CWA arsenic criterion. The court remanded the action back to EPA on May 18, 2016. The basis being EPA had not followed federal regulations for approvable CWA criteria or their own guidance regarding use of SDWA criteria under the CWA. On Sept. 14, 2016 EPA disapproved Idaho's adoption of 10 µg/L.

EPA is reevaluating the toxicological basis of its 304(a) criteria for arsenic and expects to finish in 2021. When that evaluation is finished EPA will recommend updated 304(a) criteria for arsenic and expect Idaho to adopt them, or adopt them for Idaho.

The goal of this monitoring effort is to inform criteria development by identifying arsenic levels in various Idaho waters. The following questions will be addressed:

- What are the current arsenic amounts in water and fish at locations throughout the state?
- Can arsenic data be provided to show the current background levels in waters throughout the state of Idaho?

## 5.2 Intended Use of Data

Data will be used to investigate classification of Idaho waters and to derive critical arsenic concentrations to inform guidance development. Possible classification systems to be explored may include EPA ecoregions, Idaho bioassessment site classes, or hydrological basins.

# 6 Project/Task Description

## 6.1 General Overview of Project

This QAPP addresses both phases of the project. The probabilistic arsenic accumulation phase of the project includes sampling of 24 sites during the fall dry season and water samples only during the high water spring season. This sampling will include the collection of game fish species and grab surface water samples and water quality probe data collection.

The targeted ambient arsenic in water phase of the project includes monitoring water column arsenic at 40 sites during monthly visits. The targeted sampling will include the collection of grab surface water samples and water quality probe data.

Parameters for both the probabilistic arsenic accumulation and the targeted ambient arsenic in water sampling are listed in Table 3. Physical parameters will be measured with a calibrated water quality probe. Water chemical parameters will be collected as a composited grab sample from a well-mixed area of the water body described in section 11. Biota samples will be collected by electrofishing (section 11) and composited by the lab described in section 10. Samples will be analyzed by the contract laboratory.

**Table 3. Sites will be monitored for the following physical and chemical parameters**

| Sample Type | Parameter | units |
|---|---|---|
| **Biota** | Total Arsenic | mg/kg |
| | Inorganic Arsenic | mg/kg |
| **Water Chemistry** | Total Arsenic | µg/L |
| | Inorganic Arsenic | µg/L |
| **Water Quality Meter** | Temperature | °C |
| | pH | n/a |
| | Specific conductance | µS/cm |
| | Dissolved oxygen | (mg/L or % Sat) |

## 6.2 Project Timetable

Probabilistic arsenic accumulation sampling will be performed in the fall 2019 and the spring of 2020. The fall sampling event will include the collection of fish samples, grab samples and water quality meter parameters. The spring of 2020 will only be water quality meter parameters and grab samples at the same sites (Appendix D).

Targeted ambient arsenic in water sampling will be performed for a calendar year starting in the fall of 2019. Targeted sites (Appendix E) will be sampled between August 2019 and June 2020 Monitoring results will be available for analysis by November 30, 2020. Reporting will be completed by January 31, 2021.

| Project Team | Initials | Activity |
|---|---|---|
| Jason Pappani | JP | Program Manager |
| Ian Wigger | IW | Project Manager/Sampling Lead |
| Hawk Stone | JS | Sampling assistant |
| Amanda Laib | AL | QA Officer |
| Temporary Field Staff | FS | Sampling Assistance |

| Estimated Dates | | |
|---|---|---|
| Aug 2019 – Nov 2019 | IW, HS, FS | Probabilistic fish and water quality sampling |
| Spring 2020 | IW, HS, FS | Probabilistic water sampling |
| Aug 2019 – July 2020 | IW, HS, FS | Targeted water sampling |

| | | |
|---|---|---|
| Spring 2020 | AL | Field Audit |
| Fall 2020 | IW | Data Review, Verification |
| Fall 2020 | AL | Data Validation |
| Winter 2021 | JP | Project Report |

# 7 Quality Objectives

## 7.1 Data Quality Objectives

The probabilistic arsenic accumulation phase of the project includes sampling of sites during the fall dry season with the goal of capturing 2 sets of 5 game fish (section 11). Additionally, a composited water grab sample will be collected at each of the 24 sites (section 11).. Grab samples will be collected at the same 24 sites during the following spring high water. Sampling will include water quality probe data collection.

The targeted ambient arsenic in water phase includes the collection grab samples and water quality probe data of 40 sites during monthly visits for 1 calendar year.

Bioaccumulation can be estimated as a bioconcentration factor (BCF) through laboratory studies, where organisms take up contaminants directly from the laboratory-prepared water, or as bioaccumulation factors (BAF) that are based on field studies and include dietary exposure in addition to direct uptake from water. Because they account for dietary exposure, BAFs are generally preferred over BCFs.

Samples will be analyzed for total and inorganic arsenic. The criteria BAF is dependent on the sum of the species of inorganic arsenic. The compositing of the samples could introduce oxidation of the sample, but will not change the total inorganic arsenic value.

## 7.2 Measurement Quality Objectives

Monitoring quality objectives (MQOs) for this project are described in the following sections.

### 7.2.1 Targets for Precision, bias, and sensitivity

The MQOs for project results, expressed in terms of acceptable precision, and sensitivity, are described in this section and summarized in Table 4 below. There is significant need for lower MDL's for inorganic arsenic. The current MDL for inorganic arsenic is 0.04µg/L. We are working with the laboratory to reduce the MDL to a lower level in order to better quantify the amounts of inorganic arsenic in the fish tissue and water. The lab will perform a method detection limit study which will demonstrate precision and accuracy of the method and determine the level of the MDL and MRL for the desired accredited method BAL-1009. Details on the protocol of the method detection limit study are at EDMS #2019AKL105 and #2019AKL106.

**Table 4. Measurement quality objectives (e.g., for laboratory analyses of water samples).**

| | **MQO→** | **Precision** | | **Sensitivity** |
|---|---|---|---|---|
| **Matrix** | **Parameter** | **Duplicate Samples** | **Matrix Spike-Duplicates** | **MDL or Lowest Conc. of Interest** |
| | | Relative Percent Difference (% RPD) | | Conc. Units |
| Fish Tissue | Inorganic Arsenic | 20 | 25 | 0.004 mg/kg |
| Fish Tissue | Total Arsenic | 20 | 25 | 0.009 mg/kg |
| | | | | |
| Water | Inorganic Arsenic | 20 | 25 | 0.020 µg/L |
| Water | Total Arsenic | 20 | 25 | 0.040 µg/L |

#### *7.2.1.1 Precision*

Laboratory accuracy for each analysis is determined through statistical analysis of the laboratory equipment by the laboratory; the acceptable accuracy range for the laboratory equipment will be indicated in the laboratory sheets. Any outliers from the acceptable range in percent recovery, as determined by the laboratory, will be flagged by the laboratory. Accuracy requirements for this project are ±25%. Precision will be based on field, LCS, and, if used, matrix spike duplicates, with an RPD goal of ±20%. The maximum RPD allowed for this project is ±50%.

#### *7.2.1.2 Sensitivity*

Sensitivity is a measure of the capability of a method to detect a substance. It is commonly described as a detection limit. The method detection limit (MDL) of the water and tissue for total arsenic and inorganic arsenic is listed in Table 4.

### 7.2.2 Targets for comparability, representativeness, and completeness

#### *7.2.2.1 Comparability*

Comparability is the confidence with which one data set can be compared to another data set. Using standard sampling and analytical procedures will maximize comparability. To ensure data comparability, sample collection procedures in section 11 will be consistently followed, the same analytical procedures will be used, and the same laboratory will be used to analyze the samples throughout this project.

#### *7.2.2.2 Representativeness*

Representativeness is the degree to which the sample data accurately and precisely represent site conditions. The representativeness criterion is best satisfied by confirming that sampling locations are properly selected, sample collection procedures are appropriate and consistently followed, a sufficient number of samples are collected, and analytical results meet data quality objectives. All sampling procedures will follow the sampling procedure in section11. Representativeness is evaluated during data review, verification, validation, and reconciliation efforts by comparing the combination of data accuracy, precision, measurement range, and methods and assessing other potential sources of bias, including sample holding times, reported results of blank samples, and laboratory QA review.

#### *7.2.2.3 Completeness*

Completeness is the percentage of valid data relative to the total possible data points. For data to be considered valid, it must meet all of the acceptance criteria, including accuracy and precision, and any other criteria specified by the analytical method used. The overall data quality objective for completeness for the sampling events conducted under this QAPP is 80%.

### 7.3 Acceptance criteria of quality of existing data

If the sampling event does not meet the quality assurance goal of 80%, the data will be discussed with the program manager and a course of action agreed upon. Any required departure from this goal will be justified and explained in the project records in accordance with the QMP

## 8 Special Training/Certification

The project manager is responsible for ensuring that personnel assigned to this project are appropriately trained and qualified, with the appropriate training records on file with DEQ human resources.

All work performed by DEQ personnel will be conducted in accordance with the *Idaho General Safety and Health Standards* (Division of Building Safety 2006).

Project manager and project staff will have previous surface water sampling experience and/or on-the-job training. Project manager and project staff will be familiar with the applicable sampling methods referenced in this QAPP. Other staff/interns/volunteers may assist in monitoring under the direct supervision of the Project Manager and Project Staff and will be trained according to what is required for sample collection.

## 9 Documentation and Records

Project documents will be filed electronically in the EDMS in accordance with applicable program filing procedures. The project manager is responsible for ensuring that a copy of the current approved (and signed) QAPP, with related FSPs and SOPs, is available in the EDMS. A copy of the signed signature page for the project QAPP and FSP (if used) is to be filed in the EDMS by the project manager. Preferably, the approved document, including the signed signature page, is attached to the EDMS record in PDF format.

Field personnel will use the field form (Field Forms) to document each day's activities. Information is to be recorded as follows:

- Project data must be recorded directly, promptly, and legibly.
- Field sheet entries must be initialed and dated by the person making the entry.
- Changes or corrections to field logbook notes and/or data must be indicated with a single line through the original entry. Changes must be initialed, dated, and explained.

In addition to field notes (Appendix C), documentation used to develop the monitoring network shall be filed in the EDMS and the record number recorded for the project.

All documentation necessary to support the objectives of the project and the validity of project data—chain-of-custody forms, audit reports, laboratory reports, field notes, field logbooks, etc.—shall be entered into the project EDMS files, including the supporting document record numbers. Annual project audit and assessment documentation, per the DEQ QMP, shall also be entered into the EDMS by the project QAO and/or the project manager, as applicable.

All project documentation and records shall be retained in the EDMS in accordance with the current approved DEQ records retention schedule (DEQ undated).

# 10 Sampling Process Design

## 10.1 Probabilistic Arsenic Accumulation Design

A random probability design is employed in this study (Appendix B). Sites are represented by a latitude and longitude, known as the "x-site". A draw of 24 sites from this sampling frame serves as the primary set of waters to be sampled.

Sites from this list are screened for suitability for sampling (Appendix D). Sites that are deemed unsampleable are replaced systematically. Replacement sites are taken from an 'over-sample' of additional sites drawn with the primary sites. If primary sites are eliminated as unsuitable, replacement sites from the overdraw list are taken in the order given so as to maintain a statistically valid random sample (Appendix B).

A table of probabilistic arsenic accumulation sites is included as Appendix D.

This monitoring will provide DEQ with data to allow for the calculation on a BAF to support the Arsenic Human Health criteria rulemaking. Additionally these data can be used to support future rulemaking related to background criteria.

A river sample reach is defined as 40 times the general wetted width with a minimum reach length of 150 m and maximum reach length of 4000 m. The x-site is located as near the center of the reach as is practicable.

Electrofishing will occur throughout the sample reach. In the event electrofishing the reach does not yield 5 fish per species (up to 2 species) electrofishing will continue downstream until the takeout or 5 fish per species is captured. The location and time at which electrofishing is ended will

be recorded. See the Beneficial Use Reconnaissance Program Field Manual for Rivers for detailed description of field methods (DEQ 2006)

The name of the water body and exact location (latitude and longitude) are provided with the site coordinates (Appendix D). Because capture of fish will involve moving around the water body, GPS coordinates will be obtained at the beginning and end of the reach fished.

Water samples are to be collected at 3 transects within the reach. The 3 transects are located at the top of the reach, mid reach (the "x-site" location) and the bottom of the reach. Each transects will be sampled at ¼, ½ and ¾ of the stream width giving 3 subsamples per transects and 9 total subsamples. The nine subsamples will be combined in a non-reactive vessel as a composite. Samples will be analyzed for total and inorganic arsenic. The compositing of the samples could introduce oxidation of the sample, but will not change the total inorganic arsenic value.

A fraction will then be transferred into the 60mL analysis bottle and the two 10ml vacuettes as described in section 11.

### 10.1.1 Sample Design Logistics

Sampling logistics for this project, such as sample locations and handling, are detailed below.

Fall probabilistic arsenic accumulation fish sampling will ideally be implemented as follows. However, unforeseen constraints could significantly affect the collection of fish samples. If species of targeted fish are not captured, other species are acceptable. Similarly, if the targeted size criteria are not collected then any size and quantity will suffice. If the targeted conditions are not met, then a description will be included within the notes section of the field notes.

#### *10.1.1.1 Species*

The target species is game fish typically consumed by anglers as this supports the human health criterion for fish consumption. The target fish sample is 5 game fish from each of 2 different species. Fish found floating dead or those showing skin lacerations will not be used for analysis.

#### *10.1.1.2 Size*

Fish tissue elements are expressed as a single composite of tissue from a target of five (5) individuals of the same species where the smallest individual is no less than seventy-five percent (75%) of the total length (size) of the largest individual. For example, if the largest fish were 10", then the smallest must not be less than 7.5".

#### *10.1.1.3 Processing*

Sampled fish will be identified, measured and labeled, and will be handled as detailed in section 11. Brooks Analytical Labs will prepare, process and analyze the fish samples.

#### *10.1.1.4 Sampling Times*

The time of day sampling of water and biological communities occurs is not critical but will be recorded. Likewise, although fishing success may vary throughout the day, the exact time of collection is not critical to this study.

Overall sampling is planned for August through November of 2019.

#### *10.1.1.5 Target Fish Species and Size Class*

The target species for this study in order of preference are game fish that would normally be caught by an Idaho angler**.** The goal is two game fish species from each site, but if preferred species are absent other species will be sampled at the crew's discretion.

Size of fish collected for analysis will vary based on species but all fish collected should be of legally kept size. The length and weight of each fish caught will be measured and recorded.

#### *10.1.1.6 Target Analytes*

For this study the primary analytes of concern in fish and water is total and inorganic arsenic. Arsenic is of interest because Idaho has an outdated human health criterion and efforts to update it in 2005 failed in part because of lack of information about arsenic bioaccumulation specific to species inhabiting Idaho waters. Part of the issue is the form of arsenic (inorganic or total) that bioaccumulates. Data on arsenic levels in fish tissue and water from this study should be useful to inform bioaccumulation rates pertinent to Idaho and application of or revision of current arsenic criteria in addition to providing a statewide picture of the extent of arsenic contamination in fish from Idaho's rivers.

#### *10.1.1.7 Sample Type*

Water samples will be grabs from well mixed flow. Because different forms of arsenic are being sampled each water sample will be split into one bottle and 2 vacuettes.

Most consumers in the general angling population do not eat the skin of the fish, justifying its removal for analysis, therefore analysis of skinless fillets provide a more relevant result than analysis of whole fish or fillets with skin attached.

The laboratory will remove the flesh or portion of flesh from the skin for compositing. Leaving the fish intact until preparation for analysis minimizes handling and thus contamination in the field. In the field care will be taken to avoid exposure of fish to exhaust fumes and dust and contact with metal surfaces.

Individual fish in a sample must all be of the same species and from the same waterbody, should be of similar size, and should all be collected within a 24-hour period.

If five individuals of two species cannot be obtained within a reasonable fishing effort (3-4 hours), composites may be based on less than five individuals.

#### *10.1.1.8 Fish Sample Compositing*

For this project compositing of the fish samples will occur at the contract laboratory. Sample composites will be prepared by the lab as follows:

1. Each fish will be placed in individually labeled Ziploc bags. These bags will then be put into a single labeled bag by species (space allowing). Ideally, the final sample will have 2 large bags of 5 individually bagged fish per site.
2. The fish will be inspected for integrity and allowed to thaw before processing. Compromised samples (e.g. spoiled samples, unlabeled samples) will be discarded.
3. Each fish will be rinsed with de-ionized water before proceeding with subsampling.

4. Then a ~10 gram plug (subsample) is taken from the meatiest (thickest) section of the fish using a clean scalpel. The plug is weighed and recorded in the processing log.
5. This plug will be placed in a stainless steel and glass grinder along with the other fish flesh plugs for that species and site. Repeat steps 4-6 until all five fish have been subsampled
6. The 5 plugs will then be ground until blended into a consistent paste. Typically this will take at least 120 seconds of grinding.
7. Approximately 50g of blended flesh will result. A sterile scoop will be used to transfer the blended flesh to a clean sample container.
8. Composite samples will be identified by Site # + composite code, and date processed. Field duplicates will be identified by appending FD to the composite sample ID, and processing duplicates by appending a P suffix. A laboratory ID number may also be assigned.
9. Composite samples should be refrozen if not to be digested the same day.

Duplicate processing composites will be prepared identically, from a second set of 10 gram plugs from the same set of fillets as the original sample. The remainder of the unused fillets will be discarded.

Between each sample, the blender will be cleaned with hot water and detergent, sterilized in 0.1% hydrochloric acid, and triple rinsed with de-ionized water. A new disposable scalpel and piece of aluminum foil for weighing will be used for each sample (set of up to ten fillets from one species and site). The scoop used for transferring the homogenate to its storage container may be reused with cleaning between composites.

A sample processing log will be maintained to record the time and date each set of fillets are taken from the freezer, subsample weights, and the time and date the composite is completed and returned to the freezer. On this log will also be recorded any discrepancies in field samples (samples not double bagged, or more than one species or site per cooler, apparently missing specimens, e.g. gap in numbering). The project manager will be notified of these discrepancies.

Composite tissue sample not used by the laboratory for analysis will be shipped back to DEQ within 30 days, or once no longer needed by the laboratory. These samples will be retained by DEQ for at least one year from time of sample collection.

## 10.2 Targeted Ambient Arsenic in Water Design

The selection for the targeted ambient arsenic in water sites (Appendix E) was narrowed to address data deficiencies in areas where changes to the arsenic criteria are likely to be implemented as well as addressing the potential natural background of arsenic in waters of the state. These sites were generally picked upstream of discharges but near population centers. The sites were selected to try to establish areas that had limited human influence. The proximity to populated areas should assist with accessibility, particularly during inclement weather.

Water samples will be grabs from well mixed flow. Samples will be collected either from stream bank or structures, depending on logistics and safety constraints. Because different forms of arsenic are being sampled each water sample will be split into one bottle and 2 vacuettes described in section 11.

#### *10.2.1.1 Processing*

Sampled water will be collected in the field and handled as detailed in section 11. Brooks Applied Labs will process and analyze the water samples.

#### *10.2.1.2 Sampling Times*

The time of day sampling of water and biological communities occurs is not critical but will be recorded. Likewise, although fishing success may vary throughout the day, the exact time of collection is not critical to this study.

#### *10.2.1.3 Target Analytes*

The primary analytes of concern in the targeted ambient arsenic in water phase is total and inorganic arsenic. Arsenic is of interest because Idaho has an outdated human health criterion and efforts to update it in 2005 failed in part because of lack of information about arsenic bioaccumulation specific to species inhabiting Idaho waters. Part of the issue is the form of arsenic (inorganic or total) that bioaccumulates. Data on arsenic levels in fish tissue and water from this study should be useful to inform bioaccumulation rates pertinent to Idaho and application of or revision of current arsenic criteria in addition to providing a statewide picture of the extent of arsenic contamination in fish from Idaho's rivers.

#### *10.2.1.4 Sample Type*

Water samples will be grabs from well mixed flow. Because different forms of arsenic are being sampled each water sample will be split into one bottle and 2 vacuettes.

# 11 Sample Collection

This section describes the method for the sample collection for both the targeted ambient arsenic in water and the sampling of fish and water for the probabilistic arsenic accumulation.

The targeted ambient arsenic in water sampling involves the monthly sampling of 40 sites (Appendix E) throughout the state of Idaho. Water quality meter reading will be taken at each of the targeted ambient arsenic in water site visits.

The probabilistic arsenic accumulation sampling will involve the collection of fish and water samples from 24 sites (Appendix D) that were picked at random (Appendix B). The Water quality meter reading will be taken at each of the probabilistic arsenic accumulation site visits. Water sampling will be conducted a second time during spring runoff conditions or as close to spring runoff that access will allow. These spring runoff site will be in the same locations as the fall 2019 fish and water collections occurred.

## 11.1 Probabilistic Arsenic Accumulation Sample Collection

Stream reaches will be located so that the coordinates of the site are within the delineated reach. Stream reaches will be 40 times the wetted width, with a minimum reach length of 150 m and a maximum reach length of 4000 m.

Fish for tissue analysis may be collected using boat or backpack electrofishing. Hook-and-line fishing is acceptable when conditions preclude electrofishing.

Sites will be monitored for both fish tissue and water chemistry during fall base flow conditions.

DEQ will collect a second water sample in the spring during runoff conditions or as close to spring runoff that access will allow. These spring runoff site will be in the same locations as the fall 2019 fish and water collections occurred.

### 11.1.1 Probabilistic Arsenic Accumulation Water Sample Collection

Grab samples for analysis of total and inorganic arsenic in water will be comprised of a composite of 9 samples collected throughout the reach. Water samples are to be collected at 3 transects within the reach. The 3 transects are located at the top of the reach, mid reach (the "x-site" location) and the bottom of the reach. Each transects will be sampled at ¼, ½ and ¾ of the stream width giving 3 subsamples per transects and 9 total subsamples. The nine subsamples will be combined in a non-reactive vessel, where they will be mixed. A fraction will then be transferred into the 60mL analysis bottle and the two 10mL vacuettes as described in section 11.1.4.

#### *11.1.1.1 Collecting Water Samples and Water Quality Meter Collection*

**Water samples must be delivered to the contract laboratory within 1 week of collection**.

Crews must make arrangements to have samples either hand delivered or shipped accordingly and must coordinate with the laboratory to receive and preserve samples upon receipt.

To minimize contamination, samples should be collected using standard clean-sampling procedures (the "clean–hands – dirty–hands" technique described in EPA Method 1669). If the samples are expected to be anoxic or reducing in nature, they should also be collected to minimize exposure to oxygen. Identify well-mixed portion of stream for sample collection.

- Record the relevant information on the field sheet. Record SiteID (Appendix D), Site Name, Date and Time of Collection, Name of Collector, and GPS Coordinates on field form (Appendix C). Describe relevant information regarding accessing sampling location (e.g., "from raft", "waded out from boat launch").
- Take photos of any anomalies at the sampling location or other important features.
- Facing upstream, hold calibrated water quality meter at 0.5m depth in well-mixed portion of the stream. Allow measurements to equilibrate (may take over 2 minutes), then record temperature, specific conductance, dissolved oxygen and pH on the field form (Appendix C).
- Water samples are to be collected at 3 transects within the reach. The 3 transects are located at the top of the reach, mid reach (the "x-site" location) and the bottom of the reach. Each transects will be sampled at ¼, ½ and ¾ of the stream width giving 3 subsamples per transects and 9 total subsamples.
- If in raft or sampling directly from the river (not from bridge), facing upstream, hold triple rinsed 100mL bottle from the base. Invert bottle and plunge into water to a depth of approximately 0.5 meters. Tip mouth upward toward surface. Allow bottle to fill completely, remove from the water.

- 
- Each of the subsamples will be placed in the non-reactive vessel compositing 1liter bottle.
- After completing the 9 subsamples, lightly invert the capped bottle to mix the sub-samples.
- A fraction will then be transferred into the two 10mL vacuettes as described below and the 60mL analysis bottle.
- Using pencil or indelible marker, pre-label all sample containers with the following:
    - Vacutte
    - Sample ID
    - Site location
    - Sample Date
    - Sample Time
    - Initials of collector
- Put on nitrile gloves.
- Pull the sample, avoiding agitation as much as possible
- Pull the vacuette sample first from the sample collection device, and as soon as possible to avoid oxidation of the sample.
- There will be 2 vacuette samples per site this will be from the same syringe pull described below. These vacuette vials are the inorganic arsenic samples and should be labeled accordingly.
- The vacuette sample is collected as follows:
    1. One 15mL syringe, one 0.45µm luer-lock filter, one luer-lock needle, and one 10mL vacuette container are removed from the supplied packaging. Do **not** remove the cap from the vacuette container at any time.
    2. Attach the luer-lock 0.45µm filter to the end of the syringe.
    3. Remove the plunger from the syringe.
    4. Fill the syringe with the sample to be evaluated for arsenic speciation, then replace the plunger in the syringe top.
    5. Attach the luer-lock needle to the end of the filter. Remove the sheath from the needle.
    6. Expel *and discard* 2-3mL of sample from the syringe apparatus.
    7. Carefully insert the tip of the needle through the septum in the vacuette's cap. The vacuette should fill itself, but the sampler may also gently depress the plunger to fill the container. Leaving a small amount of headspace (1 - 2mL) in the vial is acceptable.
    8. Remove the needle from vacuette, then gently invert the container several times to fully solubilize the EDTA preservative within the vacuette.
    9. Label the vacuette with the sample ID, then place the container into the supplied plastic bag. Seal the bag and place into a cooler containing ice. Log each sample on the supplied chain of custody (COC) form.
    10. Dispose of each used needle into the supplied *short-term* sharps disposal container. This container should be tightly sealed after use and returned to BAL for proper disposal.
- Pour the remaining water from the sample collection device to fill the 60mL bottle. This is

the total arsenic sample and should be labeled accordingly. For QC\QA: add "b" for blanks or "d" for duplicate to end of complete sample ID.

- Decontaminate any wading gear following the decontamination procedure outlined in the BURP field manual for streams (*www.deq.idaho.gov/media/60176695/burp-field-manual-streams.pdf*).
- Complete Laboratory Chain of Custody Form. Ship sample in cooler filled with ice. Double bag all ice in two zip-sealed plastic bags. Ship FedEx or UPS overnight to Contract Laboratory with Chain of Custody Form included.

### 11.1.2 Collecting Fish

DEQ will collect a composite of up to five individual fish from each of two species for fish tissue analysis of total and inorganic arsenic.

A raft-mounted or backpack electrofisher will be generally used to collect fish. This will be operated by trained DEQ personnel. Electro-fishing is the preferred method of capture, as it involves minimal handling of fish. However it is not effective in deep water, or for larger fish. Hook and line sampling may be used to augment electrofishing, or in the event electrofishing is not possible or effective.

DEQ will identify and measure all fish captured within the reach. When necessary, fish may be collected from beyond the reach, provided that they are captured from the same assessment unit (AU) as the x-site.

Upon capture fish will be identified for eligibility to be kept as part of the sample. For this study, 'eligible' means fish of a target species and appropriate length. The length is defined as the distance from the anterior-most part of the fish (lips) to the tip of the longest caudal fin ray. DEQ will target individuals from the two most-abundant gamefish species at each site. To control for size, the smallest fish in a composite sample must be at least 75% of the total length of the largest fish.

If the target number of individual fish from the target species are not collected, a composite sample of the fish collected will be analyzed. If no fish from the target species are collected, tissue from the species that is either most likely to be consumed, or is of a size that could be consumed will be collected.

Additional eligibility guidelines:

- Dead specimens other than those killed in the process of collection will be discarded.
- Specimens with lacerations will be discarded.
- Specimens with sores or lesions will be discarded.

Retained fish will be kept in a live well until fishing is completed. Each fish will have length measured (cm) and weight taken (gm). This information will be recorded on the field form (Appendix C).

Length of time spent fishing and general weather and water conditions should also be recorded. Weighing and measuring of each fish may be done either as fish are caught (desirable from standpoint of limiting size range) or on-shore after sampling. All sample containers will be protected in an ice chest that will be kept closed.

#### *11.1.2.1 Handling Fish and Labeling Samples*

Fish will be rinsed with ambient water immediately prior to shipping to remove any mud. It is recommended to then wipe each fish with a rag to remove slime and ease handling.

Gloves will be discarded if they contact any environmental surface, especially metal surfaces, such as the raft frame.

Each fish will be placed in its own plastic zip-lock bag. It is also desired to combine bagged fish of the same species from each site into one larger bag (e.g. kitchen garbage bag) and placed in cooler.

Fish should be packaged as quickly as possible after removal from the live well. Each fish should be carefully placed into a Ziploc bag. The full sample ID and date MUST be written in permanent marker on the outside of each bag with a waterproof marker. Pre-labeling of bags is recommended to expedite this process and usually results in more legible information.

Bagged fish will be promptly put in a cooler on ice. Samples should be frozen or placed on dry ice within 24 hours. Frozen samples may be held for up to a week for shipping. A record should be kept documenting that fish samples remain frozen.

Each site will have a designated fish cooler for fish to be sent to the lab. It is desirable that fish from different sites not be packaged in the same cooler, but this is acceptable if all the fish from each sample (5 fish per species at a site) are kept together in separate larger bags. A second cooler will be needed for water samples. Water samples must be kept cold but not frozen, i.e. on wet ice. Fish must be kept on ice or frozen until processing for analysis. If fish will be held more than twenty-four hours before shipping they should be frozen. Dry ice is needed for transporting and shipping fish.

All sample coolers will be handled and shipping to via appropriate courier, paying particular attention to pick up times and arrival time to assure sample integrity.

#### *11.1.2.2 Sample Identification Numbers*

Each bagged fish will be identified with a Sample ID number that consists of a Site # (Appendix D) + Target fish sample (A or B) + Fish # (1 through 5). Site #'s are taken from the site list (Appendix D). Example individual fish sample ID: ASP002A1 but the Sample ID is ASP002A. There should be a separate sample ID from this example site named: ASP002B. For QC\QA, add "d" for duplicate to end of complete sample ID.

If a fish is too large to fit in a single gallon-sized bag it is permissible to cut out and keep for further processing only a central (thickest) portion of the fish. This portion should be as large as will fit in a gallon sized bag. If such field sample sizing occurs it will be noted on the field form.

Note: the fish # is dropped from the Sample ID once a sample is placed in the composite bag composited. If necessary, Sample IDs will be reconciled with a laboratory-assigned sample number at a later stage.

Further field precautions:

- Coolers should be clean and washed before use.
- Regular ice is preferred to 'Blue' ice packs. Loose ice is to be avoided. Ice will be contained in large zipped bags, such that meltwater does not escape and contact the

sample containers or fish.

- Sampling equipment that is dirty will not be used.
- Measuring devices will be washed before each sampling day, and rinsed with ambient water between each species/sampling event.

All samples will be identified with date of collection and names or initials of samplers as well.

## 11.2 Targeted Ambient Arsenic in Water Sample Collection

Water samples will be grabs from well mixed flow. Because different forms of arsenic are being sampled each water sample will be split into one bottle and 2 vacuettes. The sampling will be done from either bridge or suitable access to water. The samples should be collected from a well-mixed, flowing water.

### 11.2.1 Collecting Water Samples and Water Quality Meter Collection

**Water samples must be delivered to the contract laboratory within 1 week of collection**.

Crews must make arrangements to have samples shipped accordingly and must coordinate with the laboratory to receive and preserve samples upon receipt.

To minimize contamination, samples should be collected using standard clean-sampling procedures (the "clean–hands – dirty–hands" technique described in EPA Method 1669). If the samples are expected to be anoxic or reducing in nature, they should also be collected to minimize exposure to oxygen. Identify well-mixed portion of stream for sample collection.

- Record the relevant information on the field form (Appendix C). Record SiteID (Appendix E), Site Name, Date and Time of Collection, Name of Collector, and GPS Coordinates. Describe relevant information regarding accessing sampling location (e.g., "left bank", "waded out from boat launch" "bridge").
- Take photos of any anomalies at the sampling location or other important features.
- Take water sample at approximately 0.5 meters form the surface or mid-depth if too shallow in a well-mixed part of the stream.
- Facing upstream, hold calibrated water quality meter at 0.5 m depth in well-mixed portion of the stream. Allow measurements to equilibrate (may take over 2 minutes), then record temperature (°C), specific conductance, dissolved oxygen and pH.
- Using pencil or indelible marker, pre-label all sample containers with the following:
    - Sample ID
    - Site location
    - Sample Date
    - Sample Time
    - Initials of collector
- Put on nitrile gloves.
- If sampling directly from the river (not from bridge), take sample from well mixed zone flowing part of the stream, facing upstream, hold 250mL bottle from the base. Invert bottle, remove cap from sample container, and plunge into water to a depth of approximately 0.5meter. Tip mouth upward toward surface. Allow bottle to fill completely, remove from the water. If sampling from bridge or dock, using clean, triple rinsed sampler (van dorn, bucket, dipper, bottle, etc.), take sample from well mixed zone flowing part of the stream.
- A fraction will then be transferred into the two 10mL vacuettes as described below and the 60mL analysis bottle.

- [1]Pull the sample, avoiding agitation as much as possible. Pull the vacuette sample first from the sample collection device, and as soon as possible to avoid oxidation of the sample.
- There will be 2 vacuette samples per site this will be from the same syringe pull described below. These vacuette vials are the inorganic arsenic samples and should be labeled accordingly.
- The vacuette sample is collected as follows:
    11. One 15mL syringe, one 0.45µm luer-lock filter, one luer-lock needle, and one 10mL vacuette container are removed from the supplied packaging. Do **not** remove the cap from the vacuette container at any time.
    12. Attach the luer-lock 0.45µm filter to the end of the syringe.
    13. Remove the plunger from the syringe.
    14. Fill the syringe with the sample to be evaluated for arsenic speciation, then replace the plunger in the syringe top.
    15. Attach the luer-lock needle to the end of the filter. Remove the sheath from the needle.
    16. Expel *and discard* 2-3mL of sample from the syringe apparatus.
    17. Carefully insert the tip of the needle through the septum in the vacuette's cap. The vacuette should fill itself, but the sampler may also gently depress the plunger to fill the container. Leaving a small amount of headspace (1 - 2mL) in the vial is acceptable.
    18. Remove the needle from vacuette, then gently invert the container several times to fully solubilize the EDTA preservative within the vacuette.
    19. Label the vacuette with the sample ID, then place the container into the supplied plastic bag. Seal the bag and place into a cooler containing ice. Log each sample on the supplied chain of custody (COC) form.
    20. Dispose of each used needle into the supplied *short-term* sharps disposal container. This container should be tightly sealed after use and returned to BAL for proper disposal.

- Pour the remaining water from the sample collection device to fill the 60mL bottle. This is the total arsenic sample and should be labeled accordingly. For QC\QA: add "b" for blanks or "d" for duplicate to end of complete sample ID.
- Decontaminate any wading gear following the decontamination procedure outlined in the BURP field manual for streams (*www.deq.idaho.gov/media/60176695/burp-field-manual-streams.pdf*).
- Complete Laboratory Chain of Custody Form. Ship sample in cooler filled with ice. Double bag all ice in two zip-sealed plastic bags. Ship FedEx or UPS overnight to Contract Laboratory with Chain of Custody Form included

[1] 125

## 11.3 Handling and Shipping Samples

All samples will preferably be brought back to the DEQ state office for handling and shipping. Frozen fish samples will be stored at DEQ until samples can be shipped to Brooks Applied. If logistics of field work prevent sample integrity, samples can be shipped from other courier locations. Frozen fish can be held for approximately 2 weeks for shipping, but preferably shipped weekly. Water samples will be kept in a refrigerator and shipped to Brooks Applied Water samples need to be shipped weekly and need to arrive at the lab when there is staff to receive samples. The shortest holding time, from time of filed collection, is 14 days for arsenic. This will be the limiting factor in holding water samples and therefore water samples should be sent so that they arrive at the lab at least one week prior to expiration of this holding time for the oldest sample in the batch.

Samples for analysis of arsenic in fish and water will be shipped to:

**Attn: Elizabeth Madonick**
**Brooks Applied Labs**
**18804 North Creek Parkway, Suite 100**
**Bothell WA, 98011**
**(206)-753-6141**

Samples will be collected by DEQ personnel into laboratory-supplied sampling containers (i.e., from analytical laboratory, laboratory supplier, or laboratory equipment provider), labeled, placed in an ice-chilled cooler, and transported directly to the laboratory, DEQ, or shipment location. DEQ personnel will oversee proper storage and handling of all samples collected until transferred to the appropriate analytical facility or properly discarded by DEQ. Chain-of-custody forms will be used to document sample custody and transfer. Protocols for chain-of-custody forms, sample handling, etc., are found in Appendix C. Chain-of-custody forms will accompany the samples from sample collection throughout the shipping process and shall be filed in the project EDMS system files by the project manager.

Dry ice is a must for shipping fish. Water samples should be shipped on wet ice. Double bag all ice in two zip-sealed plastic bags frozen fish on dry ice will not stay frozen more than a day during Idaho’s hot summers. Thus all shipped samples will be sent via overnight shipping. 5.5 lbs. of dry ice is usually enough to keep a cooler of fish frozen and is usually the maximum accepted by shippers. It is recommended that the ice be placed on top of the samples and excess space filled with packing material (air pillows, crumpled newspaper, etc.). Analytical results from fish samples received unfrozen or waters samples received above 4°C will be flagged as a departure from protocol.

Each cooler will have a waterproof label that specifies the site and species ID, collection date and time, and shipping date and time, as well as the contact details of the project manager (see Appendix C). The project manager will notify the laboratory of each shipment, and retain a copy of the chain of custody form. Ship FedEx overnight to Contract Laboratory with Chain of Custody Form included

# 12 Sampling Field Work Safety

Personal protective equipment (PPE) necessary to perform the field work for this project shall be consistent with the requirements of the *Idaho General Safety and Health Standards* (Division of Building Safety 2006) and all project-specific health and safety plans associated with the project.

In addition to these PPE requirements, the following specific PPE is required for field work associated with this project:

- Nitrile gloves
- Waders and Boots
- Personal Flotation Device
- Safety Lenses
- Ear protection

# 13 Analytical Methods

Large river and backpack electrofishing will be used to collect fish when possible. Samples will be collected by DEQ personnel, using the DEQ raft or backpack electrofisher. In addition, if this method is not successful or temperatures exceed the fish collection permit requirements, hook and line fishing will be used. Captured fish will be placed in a cooler which serves as a live well in the boat.

QA/QC procedures as specified for sample collection will be followed by sampling personnel. The QA/QC procedures will be fulfilled by adhering to all requirements detailed in this QAPP and the sampling procedure located in Section 11. Such adherence will be demonstrated through appropriate documentation of sampling procedures within the field logbook or field sheets as described herein. Field audits by the project QAO may also be part of QA/QC procedures.

A portable water quality meter will be used to measure pH, specific conductance, dissolved oxygen, and temperature at each sample location. If available meter doesn't include all of the parameters listed, data will be recorded with the available parameters. Unavailable parameters will be marked with "N/A" in the field notes. A GPS will be used to determine the longitude and latitude of the sampling location.

Fieldwork quality will be controlled by following the standard sampling procedure (section 11) during each sampling event, using consistent sampling containers and laboratories, and collecting sample duplicates and blanks. Procedures for all sampling events, including equipment decontamination, chain-of-custody forms, and sample blanks, are found in section 11. Detailed field notes will be taken for QC and proper sample identification. An example field notes sheet is provided in Appendix C.

Analytes, laboratories, and shipping addresses are included in section 11.3. Analytical methods, sample containers, preservation methods, and holding times are identified in section 13.

The project manager or his designee will accumulate field data sheets for entry into a database.

Surface water for both Targeted and the Probabilistic sampling will be done with the following methods.

- Total Recoverable Arsenic analysis by ICP-QQQ-MS - EPA 1638, modified with In-bottle digestion
- Arsenic Speciation analysis by EPA 1632 - Inorganic Arsenic only - Dissolved As(III), As(V), MMAs, and DMAs

Fish tissue analysis for the Probabilistic sampling will be done with the following methods.

- Total Recoverable Arsenic analysis by ICP-QQQ-MS - EPA 6020, modified with EPA 3050B digestion
- Arsenic Speciation Analysis by IC-ICP-CRC-MS Inorganic As, MMAs, and DMAs
- Total Solids (for dry-weight correction of the data)

The laboratory will apply blank corrections per laboratory SOP and note in their reports.

- EPA Method 1631 will be used to prepare fish tissue samples.

EPA Method 1632, As species, will be used for analysis of inorganic arsenic in fish tissue digests and water samples. The MDL for inorganic As is 0.004 mg/Kg in fish.

EPA Method 1638, Inductively Coupled Plasma – Mass Spectrophotometer will be used for analysis of total arsenic in fish tissue digests and water samples. The required MDL for these analytes in fish tissue is 0.05 µg/g for total. In water (blanks) the required MDLs are 0.1 µg/L for total.

Table 5lists the analytical method, container type, preservative, and holding time applicable to all samples obtained under this project. All sample containers, labels, and preservatives will be obtained from the analytical laboratory, laboratory supplier, or laboratory equipment provider. Samples must be preserved and analyzed within the holding times. The laboratory will be notified by the project manager prior to sample shipment to ensure the holding time is not exceeded. All sample collection and preparation instructions provided by the analytical laboratory will be followed throughout the duration of each project.

**Table 5. Sample container, analytical method, preservation method, and sampling holding times.**

| Parameter | Matrix | Method | Min. Mass/ Volume | Recommended Container | Recommended Preservation | Holding time |
|---|---|---|---|---|---|---|
| Trace Metals | Water | EPA 1638 Mod (ICP-MS) | 40mL | 125-mL HDPE | HNO3 in lab to pH < 2 within 14 days of collection | 6 months |
| As Species, dissolved | River Water | IC-ICP-MS (SOP #BAL-4100/4101) | 2 x 6mL | 2 x 6-mL Vacutainer (vacuette) | Field-filtration (0.45µm) into vacutainers pre-preserved with EDTA; minimal headspace; keep dark; 0-4 °C | 14 days |
| Total Metals | Wet Tissue | Various | 10g | 4-oz. glass or plastic wide mouth jars, zip-type plastic bags, or plastic wrap | 0-4 °C during shipment; ≤ -15 °C in lab | 1 year |
| As Species | Wet Tissue | IC-ICP-MS (SOP #BAL-4100/4115) | 10g | 4-oz. glass or plastic wide mouth jars, zip-type plastic bags, or plastic wrap | 0-4 °C during shipment; ≤ -18 °C in lab | 2 year |

# 14 Quality Control

Generally speaking, quality control is a means of measuring or estimating the potential variability involved with sample collection, analysis, or measurement activities in the field and in the laboratory. This section will discuss the various QC activities associated with this project.

### Field QC Checks

Field QC samples, typically duplicates and blanks, will be submitted blind (not identified as a QC sample) for analysis. The overall field QC frequency will be at least 10% of the samples (5% duplicates and 5% blanks). The fish collection field QC frequency will be 10% duplicate fish species retrieved from the same reach. Field QC sample collection will be as evenly distributed as project conditions allow.

### Sampling Quality Control

Field duplicates will be used for both water and fish. Field blanks will be generated for water samples. There are no field blanks for fish. We will test the possibility of contamination that the fish tissue compositing procedure may introduce through the use of processing blanks generated at the laboratory when the compositing takes place.

### Duplicates

Duplicate samples are two samples collected from the same location, representing the same sampling event, and carried through all assessment and analytical procedures in an identical manner. Duplicates can be “replicates” (samples taken one immediately after the other, separated only by the actual time required to fill the sample container) or “splits” (subsamples drawn from

the same initial volume of matrix). Sampling procedures outlined in section 11 will be followed for each sampling event to ensure consistency in sample collection. All relevant information will be recorded for the duplicates, just like the normal samples, in the field logbook or field sheet. Results from the field duplicate analysis will be included in the analytical report.

**Laboratory Quality Control Checks**

Laboratory QC checks are routinely performed as part of the analysis process. The frequency and type of QC samples are often analysis method-dependent and include reagent blanks, matrix spikes, and internal laboratory splits. Analyzing laboratories will report any variance from QC limits impacting the quality of sample results and may report details of internal laboratory QC if requested. The analytical laboratory may provide appropriate sample containers, chain-of-custody forms, sample labels, and any necessary container seals. Laboratory QA/QC and data reports will be filed in EDMS following applicable filing protocols.

Laboratory QC checks include internal checks for sample analysis activities, duplicate samples, and blanks. The following paragraphs describe common components of laboratory QA/QC programs.

**Laboratory Blanks** A laboratory blank is a sample of known matrix where the specific constituents requested for analysis are known to be absent or are present at concentrations less than the laboratory minimum limit of detection. The laboratory blank is analyzed to evaluate the accuracy of the analysis.

**Laboratory control samples** (LCSs) are samples that contain a known concentration of analytes and are analyzed to assess the overall method performance. They undergo the same preparatory and determinative procedures as the project samples and are the primary indicator of laboratory performance. LCS recoveries are used to measure accuracy. The RPD for duplicate LCS recoveries is used to measure precision.

A **laboratory duplicate sample** is a sample that is split by the laboratory into two separate and identical samples. The two samples are analyzed and a comparison of the results (RPD) is used to assess laboratory precision.

A **matrix spike** (MS) sample has a known amount of the target analyte added to project matrix before analysis to assess possible matrix interferences on the analysis. Percent recoveries on MS samples should be compared to percent recoveries of LCS samples. An MS/**matrix spike duplicate** (MSD) pair can be used to assess precision.

**Data Analysis Quality Control Checks** The QC check data may be checked/reviewed for quality by the project manager or the project QAO at any time during the project and must be checked after all of the data are collected. Corrective actions, as needed, will be documented in the event that control limits are exceeded. Data qualifiers will be assigned following appropriate data verification/validation procedures. Any qualifiers added will be defined in the project summary/technical report and will be consistent with EPA QA/G-8 (EPA 2002b).

# 15 Instrument/Equipment Testing, Inspection, and Maintenance

Laboratory instrument and equipment testing, inspection, and maintenance are performed and documented by the laboratory as required by the State of Idaho laboratory certification process. Procedures and schedules for preventive maintenance of sampling equipment are the responsibility of the laboratory. Each instrument or item of laboratory equipment will be maintained and assessed periodically to ensure accuracy. These procedures and frequency of performance assessment are typically designated in the individual instrument manuals.

Field instrument and equipment testing, inspection, and maintenance will be performed in accordance with the manufacturer's manual.

# 16 Instrument/Equipment Calibration and Frequency

Laboratory instrument calibration is conducted and documented by the laboratories as required by the State of Idaho laboratory certification process.

All field monitoring equipment (temperature, pH, specific conductance, dissolved oxygen, etc.) will be calibrated and maintained as recommended by the manufacturer, or as found in individual manuals, to ensure accuracy within specified limits. Calibration details will be recorded in the field logbook or field sheet. Field equipment used to collect samples will be calibrated according to manufacturers' procedures or internal guidelines at the start of each field day (at a minimum) or at intervals recommended by the manufacturer or found in individual manuals. Each instrument or item will be visually inspected by personnel for damage and operability prior to each sampling event.

# 17 Inspection/Acceptance of Supplies and Consumables

All sample containers will be obtained from the analytical laboratory. All sampling supplies and consumable items will be inspected for acceptance by the project manager prior to use.

# 18 Non-direct Measurements and External Data Acquisition

Non-direct measurements and external data acquisition refer to data obtained *for use by the project* from existing data sources, not directly measured or generated in the scope of this project. These data are often referred to as "existing or third-party data." Examples of this type of data include data obtained from existing sources or databases (either from within or from outside DEQ) and data obtained by others and offered or presented to DEQ for use in the decision-making process.

**This section describes, for all non-direct measurements and external data acquired for use by the project, the following information:**

1. **The specific source of the data**

2. **The data format**
3. **A list/description of the information or data to be acquired for use**
4. **A description of the quality program and quality assurance procedures used by the data originator when the data were originally obtained**
5. **How the data will be accessed, acquired, and managed by the project**
6. **The intended use of the information or data by the project, including how the data will be used in the project decision-making process**
7. **The specific criteria to be used for data acceptance or rejection prior to use, including what information will be used to determine if the data is of sufficient quality for use by the project**
8. **The specific criteria used to determine data use limitations.**

Project staff are strongly encouraged to review the EPA guidance for acquisition and use of non-direct measurements (external, secondary, or existing data) presented in chapter 3 of EPA QA/G-5 (EPA 2002a); the evaluation of data integrity presented in chapter 4 of EPA QA/G-8 (EPA 2002b); and the General Description of the Quality Management System Process for the Use of "External/Third Party Environmental Data" by the Idaho DEQ (DEQ 2014).

The laboratories shall provide DEQ with a data package that includes the analytical results of the submitted samples, the QA/QC report for the analyses, and a copy of the chain-of-custody record. Laboratories will be requested to provide results and reports in an electronic format.

No other non-direct data are expected to be acquired or used by this project.

# 19 Data Management

Electronic copies of all field notes and laboratory reports will be kept in EDMS. Hard copies of field notes and laboratory data reports will be kept at least until data review and reporting is complete. Additional document retention requirements may apply per project-specific, program, state, or federal requirements. It is the responsibility of the project manager to ensure all document retention requirements are met.

The analytical results for the project will be uploaded to the DEQ EDAS2 database, after review, verification, and validation is completed by the project manager and QAO, and will be available to the public through the DEQ.

# 20 Assessment and Response Actions

Assessment of the project QAPP will be performed by reviewing field notes and laboratory reports and by conducting field and laboratory audits where possible and resources allow. This assessment will be completed or directed by the QAO. Any errors or inconsistencies identified in the field notes will be investigated and corrected to ensure the integrity of the data and conformance to the QAPP. Results of internal laboratory QA review, audits, surveillances, or other types of laboratory assessments will also be taken into account. If unexpected analytical results are reported for any reason, the project manager will contact the laboratory to perform an

additional quality review of the data in question. The QAO will perform assessment of the project independently of the project manager.

A note to the file will be included with the field notes and laboratory reports if any follow-up QA activities regarding field notes or laboratory reports are required and conducted.

The QAO shall audit the QAPP annually, per the DEQ QMP (DEQ 2017), to determine if revision is necessary. The project manager should also review the project QAPP on an annual basis to ensure that the document continues to meet the needs of the data user(s). Audits and reports shall utilize the appropriate checklist forms located in Appendix A and will be documented in the EDMS, indicating the date of the audit and listing identified issues or concerns in accordance with the QMP. If the project QAPP and/or FSP requires revision as a result of this audit or review, these actions will be taken and the revised QAPP submitted for approval prior to implementation, per the DEQ QMP (DEQ 2017).

# 21 Reports to Management

Project and sample results for the Arsenic Monitoring project will be presented as supporting information in the Arsenic criteria for human health Implementation Guidance and may be used for listing decisions in the 2018 Integrated Report.

# 22 Data Review, Verification, and Validation

**Data review** is conducted (ideally by the project manager or project technical staff) to ensure that project data have been recorded, transmitted, and processed correctly. Data review is normally performed by the unit/staff generating the data.

**Data verification** is generally conducted (ideally by the project manager or project technical staff) following initial data review and is performed to evaluate the completeness, correctness, conformance, and compliance of the data against the QAPP-specified method, procedural, or contractual requirements. The purpose of data verification is to evaluate the extent to which the sample collection requirements, analytical processes prescribed in the QAPP, and specified project procedures were followed. Data verification essentially evaluates the actual project performance against the requirements established in the QAPP. The output from this process is considered and evaluated during the reconciliation with user requirements (assessment) phase. Data verification is normally performed by the unit/staff generating the data.

**Data validation** shall be conducted by the project QAO or a subject matter expert not otherwise assigned to the project or unit generating data. This process shall follow data review and verification and is an analyte- and sample-specific process that extends the data evaluation beyond method, procedure, or contractual compliance to determine the quality of a specific data set relative to the end use. This effort should focus on the project-specific data needs and note any potentially unacceptable departures from the QAPP. The output from this process is considered and evaluated during the reconciliation with user requirements (assessment) phase.

**Data review, verification, and validation tasks are assigned to specific project staff, such as the project manager or project QAO, in section 23 of the project QAPP.**

The level of documentation required for a specific project data review, verification, validation, and reconciliation effort is specified below. This level of documentation is determined by the project manager, in consultation with the program or regional manager, consistent with the "graded approach" used by DEQ in implementing the quality management system (QMS).

Those assigned to perform project data review, verification, and validation *shall use the associated checklist provided in the appendices to perform and document* the effort in the associated project EDMS file. The checklists are also available as stand-alone documents in the DEQ EDMS as follows: data review (record 2012AEB2), data verification (record 2012AEB3), and data validation (record 2012AEB4).

# 23 Review, Verification, and Validation Methods

Data review, verification, and validation efforts are based on the analytical support determined to be necessary in the planning stages of the project. DEQ personnel performing data verification and validation are encouraged to review the following guidance documents:

- EPA QA/G-8 (EPA 2002b) for guidance on methods for this task.

**Review** of data and information collected under this QAPP shall be performed by the project manager using the data review checklist found in Appendix A. This review will also include evaluation of supplied laboratory data reports. Data review will include the following activities, at a minimum:

- An examination of project data, identifying errors or undocumented changes in data entry, storage, calculation, reduction, transformation, or transcription.
- An examination to ensure all required sample information is documented and available, in preparation for the verification, validation, and assessment processes. This includes pertinent project information concerning blanks, matrixes, temperature requirements, duplicates, preservatives, shipping dates, holding times, chain-of-custody records, etc.
- An examination to identify if all required external data (non-direct measurement data) information *and supporting documentation*, as required by the project QAPP, have been received and are available for the verification and validation processes.
- A determination if any data deficiencies exist, such as missing data or compromised data integrity, due to issues such as loss in acquisition, storage, or processing.
- An examination to ensure all necessary analytical laboratory support documentation, as set forth and stipulated in the project QAPP (and FSP, if used), have been received from the applicable laboratories.
- An examination to identify programming, data entry, or software related errors, if applicable to the project.

**Verification** of data and information collected under this QAPP shall be performed by the project manager using the data verification checklist found in Appendix A. The general focus of the process is to identify if all requirements specified in the project QAPP, associated procedures, and project contractual requirements (if applicable), have been met, and if not, to

determine the extent to which requirements failed to be achieved. Data verification will include the following activities, at a minimum:

- Verification that all data completeness criteria, as stated in the project QAPP, have been satisfied. This shall include items such as the number of samples, number of QC samples such as spikes and duplicates, and chain-of-custody record continuity.
- Verification that the values of individual data points, and/or comparison calculations such as RPD, meet the criteria specified in the QAPP.
- Verification that the required analytical methods, as listed in the project QAPP, correspond to the analytical methods employed by the laboratory, as recorded in laboratory reports.
- Verification that QAPP requirements relative to laboratory analytical support documentation have been satisfied by the reporting laboratory, including the correct application of data qualifiers.
- Verification that all supporting information and documentation for external data (non-direct measurement data) meet the requirements of the QAPP. If not, identify any limitations or restriction on the use of such data.
- Verification that data and sample collection practices adhered to procedural requirements, to include a review of project logs and field notes, as applicable.
- Verification that sample handling activities conform to QAPP (and FSP, if used) requirements. Examples include sample shipment timelines, sample holding times, preservatives, number of samples obtained, duplicate or split sample frequency, and chain-of-custody documentation.
- Verification that data calculation and handling activities conform to QAPP (and FSP, if used) requirements. Examples include correct use of mathematical formulas, numerical methods, programs and programing, and correct application and documentation of database editing and information transfers.
- Verification that any remaining or unique project QAPP (and FSP, if used) or procedural requirements have been met, and if not, determine and document the extent to which these requirements failed to be achieved.
- Determine and document any limitations on the use of the project data.

**Validation** of data and information collected under this QAPP shall be performed by the project QAO using the data validation checklist found in Appendix A. The general focus of the process is to identify if the quality of the project data meets the needs of the end user and the associated decision makers.

**The data validation effort for this project shall include a minimum of 10% of all project data with a goal of 20%, except as noted specifically below.** Data validation will include the following activities, at a minimum:

- An evaluation and examination of all (100%) of obtained field QC sample results, such as duplicates and trip blanks, etc., followed by assignment (if necessary) of appropriate data qualifiers to these data based on project criteria.
- A review of project analytical laboratory reports and data, including the assigned data qualifiers, to evaluate the data quality with respect to the project DQOs. Assign data qualifiers to individual data values as necessary and appropriate.

- A review of the outcome of the data verification effort to evaluate the impact on data quality with respect to the DQOs.
- A determination, when necessary and where possible, of the reasons for any failure to meet methodological, procedural, or contractual requirements and an evaluation of the impact of such failure on the overall data.
- A comparison of the project DQOs, as defined in the project QAPP (and FSP, if used), to the data obtained by the project to assess the adequacy of the data (new or external) in relation to their intended use.
- A determination of the extent to which any external data (non-direct measurement data), and the accompanying supporting information and documentation, meet the requirements of the data user. Specifically, does the quality of the existing data adequately support the needs of the project and support the intended use of the data for the project.
- Determine and document any limitations on the use of the project data.
- Determine the adequacy of the data to proceed on to the data assessment and reconciliation with user requirements phase.

Any potentially unacceptable departures from the requirements of the project QAPP will be noted during the data review, verification, and validation process. If the project manager or the project QAO determines the data do not meet the needs of the project or the DQOs of the QAPP and/or if the conclusions drawn from the data do not appear to be reasonable, the project manager and the QAO shall immediately report such findings to the appropriate regional manager and/or State Office program manager to determine the necessary corrective actions. Documentation of such findings and activities shall be maintained in accordance with the DEQ QMP.

# 24 Reconciliation with User Requirements

Data quality assessment (DQA) will be performed in accordance with this QAPP and the DEQ QMP (DEQ 2017). Additional guidance for conducting data assessment can be found in EPA QA/G-9R or EPA QA/G-9S (EPA 2006a, b).

The DQA will be performed (at a minimum) by the project manager and the project QAO to determine if the project data set is of the right type, quality, and quantity to achieve the objectives of the project and can confidently be used to make an informed decision.

Information and findings associated with the project data review, verification, and validation efforts shall be considered during the data assessment process.

When DQOs are not met, the project manager will discuss appropriate corrective actions with project staff, project management, and with the analytical laboratory. Corrective actions may be initiated to suggest improvements to data collection activities, data and sample handling techniques, internal laboratory quality procedures, etc., to solve quality issues.

If the project manager or the QAO decide the project data do not meet the project needs or the QAPP quality objectives or if the conclusions drawn from the data do not appear to be reasonable, the project manager and the QAO shall immediately report such findings to the

appropriate regional manager and/or State Office program manager to determine and document the necessary corrective actions.

If sampling activities require revision, the project QAPP will be revised as necessary. Following revision, and prior to implementation, the revised project QAPP must be re-approved in accordance with the DEQ QMP (DEQ 2017).

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# 25 References

DEQ (Idaho Department of Environmental Quality). Undated (current version). "Retention Schedule." Boise, ID: DEQ. EDMS # 2010AIC3.

DEQ (Idaho Department of Environmental Quality). 2014. General Description of the Quality Management System Process for the Use of "External/Third Party Environmental Data" by the Idaho DEQ. Boise, ID: DEQ. EDMS # 2014AEC28.

DEQ (Idaho Department of Environmental Quality). 2017. Quality Management Plan. Boise, ID: DEQ. EDMS # 2016AEC7. Available at http://deq.intranet/quality-management/administrative-resources.aspx

DEQ (Idaho Department of Environmental Quality). 2018a. General Safety Manual. Boise, ID: DEQ. EDMS # 2015AEH1.

EPA (US Environmental Protection Agency). 2002b. Guidance on Environmental Data Verification and Data Validation (EPA QA/G-8). Washington DC: EPA, Office of Environmental Information. EPA/240/R-02/004. Available at http://www.epa.gov/quality/qs-docs/g8-final.pdf.

# Appendix A. Project Checklists

All checklists in this appendix are available for download and use by project staff as standalone electronic documents, from either the DEQ EDMS or the DEQ Quality System website: http://deq.intranet/quality-management/administrative-resources.aspx. Prior to using an activity checklist, project staff should review the applicable requirements listed in the project QAPP and the QMP.

The following checklists are included in this appendix:

- Data Review—EDMS # **2012AEB2**
- Data Verification—EDMS # **2012AEB3**
- Data Validation—EDMS # **2012AEB4**
- Project QAO Annual Audit—EDMS # **2012AEB5**

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# DEQ QAPP/FSP Checklist—Data Review

The individual(s) assigned in the project QAPP/FSP to perform **data review** *shall complete and file this checklist in the appropriate project electronic document management system (EDMS) file.* Project personnel are encouraged to expand this standard list, as project conditions warrant.

| Printed Name of Staff Performing Data Review | Date Completed |
|---|---|
| Project QAPP/FSP Title | QAPP/FSP EDMS Record # |

**Check the following review boxes after completion of each listed task.**

**Check *yes* if the task was completed without any noted discrepancies. Otherwise, check *no* and include a description of the discrepancy in the space provided. Use additional sheets as necessary.**

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Verify that the approved current project quality assurance project plan (QAPP), including a copy of the signed approval signature page, is currently filed in the EDMS. Also, verify the project information has been entered into the quality assurance officer (QAO) project tracker found at EDMS # **2012AEB8**. If the QAPP is not filed in the EDMS, or the QAO tracker is not current, immediately inform the DEQ quality manager. |
| ☐ | ☐ | If the project utilizes a field sampling plan (FSP), verify that the approved project FSP, including a copy of the signed approval signature page, is currently filed in the EDMS. Also, verify the project information has been entered into the QAO project tracker found at EDMS # **2012AEB8**. If the FSP is not filed in the EDMS, or the QAO tracker is not current, immediately inform the DEQ quality manager. |
| ☐ | ☐ | Examine and review the project QAPP (and FSP, if used) to determine if additional project-specific data *review* requirements apply. Update this checklist to include all such items. |
| ☐ | ☐ | Examine project data, identifying errors or undocumented changes in data entry, storage, calculation, reduction, transformation, or transcription. |

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Ensure all required sample information is documented and available, in preparation for the verification, validation, and assessment processes. This includes pertinent project information concerning blanks, matrixes, temperature requirements, duplicates, preservatives, shipping dates, holding times, chain-of-custody records, etc. |
| ☐ | ☐ | Identify if all required external (non-direct measurement) data, information, *and supporting documentation*, as required by the QAPP (and FSP, if used), have been received and are available for the verification and validation processes. |
| ☐ | ☐ | Determine if any data deficiencies exist, such as missing data or compromised data integrity, due to issues such as loss during acquisition, storage, editing, or processing. |
| ☐ | ☐ | Ensure all necessary analytical laboratory support documentation, as set forth and stipulated in the project QAPP (and FSP, if used), have been received from the applicable laboratories. |
| ☐ | ☐ | Identify programming, data entry, or software related errors, if applicable to the project. |
| ☐ | ☐ | Ensure that all deficiencies or conditions adverse to quality determined during the data *review* process have been communicated to project management and are listed on this checklist or attached for inclusion in the EDMS. |
| ☐ | ☐ | Verify that a copy of this data review checklist has been provided to the project manager for deficiency resolution and placed in the project EDMS file. Note that additional administrative actions may be required based on the review findings, such as development of a corrective action plan, report, etc. The project manager shall consult the DEQ Quality Management Plan and proceed accordingly. |

Please list any additional comments below. Attach additional sheets as necessary.

# DEQ QAPP/FSP Checklist—Data Verification

The individual(s) assigned in the project QAPP/FSP to perform **data verification** *shall complete and file this checklist in the appropriate project electronic document management system (EDMS) file.* Project personnel are encouraged to expand this standard list, as project conditions warrant.

| Printed Name of Staff Performing Data Verification | Date Completed |
|---|---|
| Project QAPP/FSP Title | QAPP/FSP EDMS Record # |

**Check the following review boxes after completion of each listed task.**

**Check *yes* if the task was completed without any noted discrepancies. Otherwise, check *no* and include a description of the discrepancy in the space provided. Use additional sheets as necessary.**

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Examine and review the quality assurance project plan (QAPP), and field sampling plan (FSP) if used, to determine if additional project-specific data *verification* requirements apply. Update this checklist to include all such items. |
| ☐ | ☐ | Verify that all data completeness criteria, as stated in the QAPP (and FSP, if used), have been satisfied. This shall include items such as the number of samples, number of quality control samples such as spikes and duplicates, and chain-of-custody record continuity. |
| ☐ | ☐ | Verify that the values of individual data points and any comparison calculations such as relative percent difference, meet the QAPP (and FSP, if used) specifications. |
| ☐ | ☐ | Verify that the required analytical methods, as listed in the QAPP (and FSP, if used) correspond to the analytical methods employed by the laboratory, as recorded in laboratory reports. |
| ☐ | ☐ | Verify that QAPP (and FSP, if used) requirements relative to laboratory analytical support documentation have been satisfied by the reporting laboratory, including the correct application of data qualifiers. |
| ☐ | ☐ | Verify that all supporting information and documentation for external (non-direct measurement) data meet the requirements of the QAPP (and FSP, if used). If not, identify any limitations or restriction on the use of these data. |

| Yes | No | |
|---|---|---|
| | | _____<br>_____<br>_____ |
| ☐ | ☐ | Verify that data and sample collection practices adhered to procedural requirements, to include a review of project logs and field notes, as applicable.<br>_____<br>_____<br>_____ |
| ☐ | ☐ | Verify that sample handling activities conform to QAPP (and FSP, if used) requirements. Examples include sample shipment timelines, sample holding times, preservatives, number of samples obtained, duplicate or split sample frequency, and chain-of-custody documentation.<br>_____<br>_____<br>_____ |
| ☐ | ☐ | Verify that data calculation and handling activities conform to QAPP (and FSP, if used) requirements. Examples include correct use of mathematical formulas and numerical methods, correct use of programs and programing, and correct application of database information transfers.<br>_____<br>_____<br>_____ |
| ☐ | ☐ | Verify that any remaining or unique QAPP (and FSP, if used) or procedural requirements have been met, and if not, determine the extent to which these requirements failed to be achieved.<br>_____<br>_____<br>_____ |
| ☐ | ☐ | Determine and document any limitations on the use of the project data.<br>_____<br>_____<br>_____ |
| ☐ | ☐ | Ensure that all deficiencies or conditions adverse to quality determined during the project data *verification* process have been communicated to project management and are listed on this checklist or attached for inclusion in the EDMS.<br>_____<br>_____<br>_____ |
| ☐ | ☐ | Verify that a copy of this data verification checklist has been provided to the project manager for deficiency resolution and placed in the project EDMS file. Note that additional administrative actions may be required based on the verification findings, such as development of a corrective action plan, report, etc. The project quality assurance officer shall consult the DEQ Quality Management Plan and proceed accordingly.<br>_____<br>_____<br>_____ |

Please list any additional comments below. Attach additional sheets as necessary.

_____

# DEQ QAPP/FSP Checklist—Data Validation

The individual(s) assigned in the QAPP/FSP to perform **data validation** *shall complete and file this checklist in the appropriate project electronic document management system (EDMS) file.* Project personnel are encouraged to expand this standard list as project conditions warrant.

Printed Name of Staff Performing Data Validation

Date Completed

Project QAPP/FSP Title

QAPP/FSP EDMS Record #

**Check the following review boxes after completion of each listed task.**

**Check *yes* if the task was completed without any noted discrepancies. Otherwise, check *no* and include a description of the discrepancy in the space provided. Use additional sheets as necessary.**

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Verify that the approved and current quality assurance project plan (QAPP), including a copy of the signed approval signature page, is currently filed in the EDMS. Also, verify the project information has been entered into the quality assurance officer (QAO) project tracker found at EDMS # **2012AEB8**. If the QAPP is not filed in the EDMS, or the QAO tracker is not current, immediately inform the DEQ quality manager. |
| ☐ | ☐ | If the project utilizes a field sampling plan (FSP), verify that the approved project FSP, including a copy of the signed approval signature page, is currently filed in the EDMS. Also, verify the project information has been entered into the QAO project tracker found at EDMS # **2012AEB8**. If the FSP is not filed in the EDMS, or the QAO tracker is not current, immediately inform the DEQ quality manager. |
| ☐ | ☐ | Examine and evaluate the project QAPP (and FSP, if used) to determine if additional project-specific data *validation* requirements apply. Update this checklist to include all such items. |
| ☐ | ☐ | Examine and evaluate all (100%) of obtained field quality control sample results (i.e. duplicates, trip blanks, etc.) followed by assignment (if necessary) of appropriate data qualifiers to these data based on project criteria. |
| ☐ | ☐ | Assess project analytical laboratory reports and data, including the assigned data qualifiers, to evaluate the data quality with respect to the project data quality objectives (DQOs). Assign and document data qualifiers to individual data values as necessary and appropriate. |

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Evaluate the outcome of the data verification effort and assess the impact on data quality with respect to the DQOs. |
| ☐ | ☐ | Determine, when necessary and where possible, the reasons for any failure to meet methodological, procedural, or contractual requirements and evaluate the impact of such failure on overall data quality. |
| ☐ | ☐ | Compare the project DQOs, as defined in the QAPP (and FSP, if used), to the data obtained to assess the adequacy of the data (new or external) in relation to their intended use. |
| ☐ | ☐ | Determine the extent to which any external (non-direct measurement) data, and the accompanying supporting information and documentation, meet the requirements of the end user. Specifically, does the quality of the data adequately support the needs of the project and support its intended use? |
| ☐ | ☐ | Determine and document any limitations on the use of the data. |
| ☐ | ☐ | Determine the adequacy of the data to proceed on to the data-assessment and reconciliation-with-user-requirements phases. |
| ☐ | ☐ | Ensure that all deficiencies or conditions adverse to quality determined during the project data *validation* process have been communicated to project management and are listed on this checklist or attached for inclusion in the EDMS. |
| ☐ | ☐ | Verify that a copy of this data validation checklist has been provided to the project manager for deficiency resolution and placed in the project EDMS file. Note that additional administrative actions may be required based on the validation findings, such as development of a corrective action plan, report, etc. The project QAO shall consult the DEQ Quality Management Plan and proceed accordingly. |

Please list any additional comments below. Attach additional sheets as necessary.

# DEQ QAPP/FSP Checklist—Annual QAO Project Audit

The individual assigned in the QAPP/FSP as the quality assurance officer (QAO) shall audit the project on at least an annual basis. The QAO *shall complete this checklist as part of the audit process and file the completed form in the appropriate project electronic document management system (EDMS) files.* QAOs are encouraged to expand this standard list as project conditions warrant.

Printed Name of Staff Performing the QAO Audit

Date Completed

Project QAPP/FSP Title

QAPP/FSP EDMS Record #

**Check the following review boxes after completion of each listed task.**

**Check *yes* if the task was completed without any noted discrepancies. Otherwise, check *no* and include a description of the discrepancy in the space provided. Use additional sheets as necessary.**

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Verify that the approved current project quality assurance project plan (QAPP) and field sampling plan (FSP) if used, including a copy of the signed approval signature page, is currently filed in the EDMS. Also, verify the project information for the QAPP (and FSP, if used) has been entered into the QAO project tracker found at EDMS # **2012AEB8**. If the QAPP (and FSP, if used) are not filed in the EDMS, or the QAO tracker is not current, immediately inform the DEQ quality manager. |
| ☐ | ☐ | Verify that the approved and current project documents, such as the QAPP (and FSP, if used), standard operating procedures (SOPs), etc., are available to project staff and are in use per project requirements. |
| ☐ | ☐ | Determine through review and observation if the project has performed and documented activities as described and required by the QAPP (and FSP, if used) such that the needs of the data user are satisfied. |
| ☐ | ☐ | Determine if the QAPP (and FSP, if used) adequately document and describe the actual project requirements such that the needs of the data user are satisfied. If necessary, in coordination with the project manager, initiate project document revision, review, and approval efforts in accordance with the DEQ Quality Management Plan (QMP). |

| Yes | No | |
|---|---|---|
| ☐ | ☐ | Determine if the project analytical requirements are adequately met by the selected laboratory, including use of proper analytical methods and sufficient analytical data support documentation. |
| ☐ | ☐ | Determine if project sample handling activities are in compliance with the requirements of the QAPP (and FSP, if used). |
| ☐ | ☐ | Determine if project field activities are in compliance with the requirements of the QAPP (and FSP, if used). |
| ☐ | ☐ | Determine if all external (non-direct measurement) data acquisition associated with the project has been addressed and properly documented in the QAPP (and FSP, if used). |
| ☐ | ☐ | Compare actual project documents available in the EDMS against the document filing requirements contained in the QAPP (and FSP, if used). Identify existing deficiencies in the project EDMS files, such as missing field note pages and missing chain-of-custody forms, and provide this information to the project manager for immediate resolution. |
| ☐ | ☐ | Ensure that all deficiencies or conditions adverse to quality determined during the project QAO audit process are listed on this checklist or attached for inclusion in the EDMS. |
| ☐ | ☐ | Verify that a copy of this annual QAO audit report has been provided to the project manager for deficiency resolution and placed in the project EDMS file. Note that additional administrative actions may be required based on audit findings, such as development of a corrective action plan, report, etc. The QAO shall consult the DEQ QMP and proceed accordingly. |

Please list any additional comments below. Attach additional sheets as necessary.

# Appendix B. Description of Survey Design

**Target population:** All streams and rivers within Idaho excluding streams on Native American Reservations and Wilderness areas.

**Sample Frame:** DEQ provided the shapefile that was used as basis for the sample frame (305bPerennielStreamsC). All perennial streams were included. Streams that occur on Native American Reservations and Wilderness areas were excluded.

**Survey Design:** A Generalized Random Tessellation Stratified (GRTS) survey design for a linear resource was used. The GRTS design includes reverse hierarchical ordering of the selected sites.

**Multi-density categories:** Categorized by stream size based on Strahler Order (Small = 1st – 5th, Large = 6th – 8th), with unequal probability selection.

**Stratification:** Stratified by six Idaho administrative basins (Bear, Clearwater, Panhandle, Salmon, Southwest, and Upper Snake).

**Panels:** None.

**Expected sample size:** Total of 24 sites.

**Over sample:** 500% (120 sites) for a total of 144 sites.

**Site Use:** Sites are listed in siteID order and must be used in that order within each stratum (administrative basin). All sites that occur prior to the last site used must have been evaluated for use and then either sampled or reason documented why that site was not used. As an example, if 24 sites are to be sampled and it required that 50 sites be evaluated in order to locate 24 sites able to be sampled, then the first 50 sites in siteID order would be used.

**Sample Frame Summary**
Stream and River length in kilometers

| Name | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| **Bear River** | 292 | 332 | 189 | 82 | 85 | 124 | 0 | 0 |
| **Clearwater** | 1901 | 1351 | 806 | 509 | 278 | 16 | 0 | 0 |
| **Panhandle** | 2046 | 1376 | 782 | 330 | 230 | 1 | 0 | 2 |
| **Salmon** | 3628 | 2037 | 1221 | 499 | 284 | 185 | 121 | 0 |
| **Southwest** | 3035 | 1843 | 1386 | 751 | 386 | 643 | 10 | 21 |
| **Upper Snake** | 4068 | 2367 | 1654 | 1254 | 747 | 653 | 26 | 0 |

| Name | 1st_5th | 6th_8th | Sum |
|---|---|---|---|
| **Bear River** | 1863.26 | 142.86 | 2006.11 |
| **Clearwater** | 10515.32 | 25.35 | 10540.7 |
| **Panhandle** | 9701.06 | 4.27 | 9705.33 |
| **Salmon** | 17047.26 | 296.37 | 17343.6 |
| **Southwest** | 14786.02 | 530 | 15316 |
| **Upper Snake** | 15547.21 | 574.1 | 16121.3 |
| **Sum** | 69460.13 | 1572.95 | 71033.1 |

**Site Selection Summary**

**Description of Sample Design Output**
The output is provided as a shapefile for the sites. Note that the ".dbf" file may be read in Excel.

The attributes are as follows:

| | |
|---|---|
| SiteID | Unique site identification (character) |
| xcoord | x-coordinate from map projection |
| ycoord | y-coordinate from map projection |
| mdcaty | Multi-density categories used for unequal probability selection |
| wgt | Weight (in km), inverse of inclusion probability, to be used in statistical analyses |
| stratum | Strata used in the survey design |
| panel | Identifies base sample by panel name and Oversample by OverSamp |
| EvalStatus | Site evaluation decision for site: TS: target and sampled, |

| | |
|---|---|
| | LD: landowner denied access, etc. (see below) |
| EvalReason | Site evaluation text comment |
| auxiliary variables | Remaining columns are from the sample frame provided |

**Evaluation Process**

The survey design weights that are given in the design file assume that the survey design is implemented as designed. Typically, users prefer to replace sites that cannot be sampled with other sites to achieve the sample size planned. The site replacement process is described above. When sites are replaced, the survey design weights are no longer correct and must be adjusted. The weight adjustment requires knowing what happened to each site in the base design and the over sample sites. EvalStatus is initially set to "NotEval" to indicate that the site has yet to be evaluated for sampling. When a site is evaluated for sampling, then the EvalStatus for the site must be changed. Recommended codes are:

| EvalStatus Code | Name | Meaning |
|---|---|---|
| TS | Target Sampled | site is a member of the target population and was sampled |
| LD | Landowner Denial | landowner denied access to the site |
| IA | Inaccessible | physical barrier or distance prevented access to the site |
| NT | Non-Target | site is not a member of the target population, i.e., not a stream or river (may be marsh, dry channel, etc.) |
| NN | Not Needed | site is a member of the over sample and was not evaluated for sampling |
| Other codes | | Many times useful to have other codes. For example, rather than use NT, may use specific codes indicating why the site was non-target. |

## Statistical Analysis

Any statistical analysis of data must incorporate information about the monitoring survey design. In particular, when estimates of characteristics for the entire target population are computed, the statistical analysis must account for any stratification or unequal probability selection in the design. Procedures for doing this are available from the Aquatic Resource Monitoring web page given in the bibliography. A statistical analysis library of functions is available from the web page to do common population estimates in the statistical software environment R.

# Appendix C. Field Forms

# 2019-2020 Arsenic Monitoring Field Form

**Location Information**

Stream Name: _____ Date: _____
Location Description: _____ Time: Start: _____ Finish: _____
Site ID: _____ Staff: _____
Project Phase: _____ Targeted _ or _ Probabilistic (circle one)

**Water Quality Parameters**

Temperature: _____ ˚C _____ DO: _____ mg/L
Conductivity: _____ µS/cm _____ pH: _____ units

**Water Samples**:

- ☐ 2x10mL Filtered Vacuette (label vial with site ID and complete label on bag)
- ☐ 60mL Unfiltered (label bottle with site ID and complete label on bag and initial)

Placed in cooler # _____

**Fish Samples**

Place each individual fish in a back then the five fish from each group into large bag.
Label individual bags with Sample Id + AorB and fish number 1-5 and date.
Label the large bag with 5 fish with the site ID, the date, and the species name.
Naming Convention for sample ID for fish: ASP001A1
QC\QA: add "b" for blanks or "d" for duplicate to end of complete sample ID

Collection method:

- ☐ Species A: _____ Placed in cooler # _____
  Lengths: 1: _____ /2: _____ /3: _____ /4: _____ /5: _____
  Weights: 1: _____ /2: _____ /3: _____ /4: _____ /5: _____
  # of fish: _____
- ☐ Species B: _____ Placed in cooler # _____
  Lengths: 1: _____ /2: _____ /3: _____ /4: _____ /5: _____
  Weights: 1: _____ /2: _____ /3: _____ /4: _____ /5: _____
  # of fish: _____

**Notes**

# Cooler Contents and Chain of Custody Form

Cooler Number: _____

**Contents:**

| Site ID | Filtered Water | Unfiltered Water | Fish Species A | Fish Species B |
|---|---|---|---|---|
| | (mark with an 'X') | | | |
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Cooler contents packed by: _____ Date: _____

Cooler received by: _____ Date: _____

Contents verified by: _____ Date: _____

*This form, or a copy, must be returned to the project manager and filed in TRIM*

# Brooks Applied Laboratories Analysis Form

# Appendix D. Probabilistic Monitoring Site Locations

| Site ID | Stream Name | Basin | Method | Latitude | Longitude |
|---|---|---|---|---|---|
| ASP002 | Hillyard Canyon | Bear River | Backpack | 42.136 | -111.635 |
| ASP004 | Bear River | Bear River | Raft | 42.058 | -111.919 |
| ASP005 | Bear River | Bear River | Raft | 42.438 | -111.381 |
| ASP007 | Whiskey Creek | Bear River | Backpack | 42.465 | -111.709 |
| ASP008 | Maple Creek | Bear River | Backpack | 42.035 | -111.759 |
| ASP009 | Bear River | Bear River | Raft | 42.579 | -111.494 |
| ASP010 | Bear River | Bear River | Raft | 42.256 | -111.301 |
| ASP012 | Twomile Creek | Bear River | Backpack | 42.158 | -112.166 |
| ASP026 | Warm Springs Creek | Clearwater | Backpack | 46.466 | -114.876 |
| ASP027 | Red River | Clearwater | Backpack | 45.792 | -115.456 |
| ASP031 | Cranberry Creek | Clearwater | Backpack | 46.635 | -116.140 |
| ASP035 | Potlatch River | Clearwater | Backpack | 46.612 | -116.655 |
| ASP036 | East Fork Potlatch River | Clearwater | Backpack | 46.891 | -116.226 |
| ASP039 | Potlatch River | Clearwater | Backpack | 46.598 | -116.679 |
| ASP042 | Slide Creek | Clearwater | Backpack | 46.084 | -115.450 |
| ASP043 | Orofino Creek | Clearwater | Backpack | 46.496 | -115.979 |
| ASP051 | Saint Joe River | Panhandle | Raft | 47.219 | -115.575 |
| ASP052 | Hayden Creek | Panhandle | Backpack | 47.823 | -116.654 |
| ASP055 | Trib to John Creek | Panhandle | Backpack | 47.154 | -116.695 |
| ASP056 | North Fork Coeur d'Alene River | Panhandle | Backpack | 48.026 | -116.252 |
| ASP060 | Keller Creek | Panhandle | Backpack | 47.715 | -115.995 |
| ASP062 | Rock Creek | Panhandle | Backpack | 47.259 | -115.891 |
| ASP065 | Gillon Creek | Panhandle | Backpack | 48.979 | -116.223 |
| ASP066 | Schweitzer Creek | Panhandle | Backpack | 48.356 | -116.595 |
| ASP076 | Salmon River | Salmon | Raft | 45.331 | -114.366 |
| ASP077 | trib to Gold Creek | Salmon | Backpack | 44.117 | -114.827 |
| ASP084 | Little Slate Creek | Salmon | Backpack | 45.481 | -116.101 |
| ASP088 | South Fork Salmon River | Salmon | Raft | 45.215 | -115.545 |
| ASP090 | Salmon River | Salmon | Raft | 44.595 | -114.189 |
| ASP091 | Seafoam Creek | Salmon | Backpack | 44.542 | -115.078 |
| ASP092 | Tributary to Skookumchuck Creek | Salmon | Backpack | 45.701 | -116.196 |
| ASP093 | Salmon River | Salmon | Raft | 45.386 | -114.054 |
| ASP098 | Little Canyon Creek | Southwest | Backpack | 43.020 | -115.296 |
| ASP100 | Granite Creek | Southwest | Backpack | 43.813 | -115.404 |
| ASP102 | Marys Creek | Southwest | Backpack | 42.227 | -115.949 |
| ASP104 | Mores Creek | Southwest | Backpack | 43.651 | -115.981 |
| ASP105 | Weiser River | Southwest | Raft | 44.255 | -116.773 |
| ASP109 | Payette River | Southwest | Raft | 43.985 | -116.786 |
| ASP110 | Grouse Creek | Southwest | Backpack | 43.567 | -115.194 |
| ASP111 | Tributary to Cascade Reservoir | Southwest | Backpack | 44.743 | -116.150 |
| ASP122 | Snake River | Upper Snake | Raft | 43.661 | -111.723 |
| ASP123 | Rock Creek | Upper Snake | Backpack | 42.551 | -114.479 |
| ASP125 | Moody Creek | Upper Snake | Backpack | 43.744 | -111.640 |
| ASP126 | Henrys Fork | Upper Snake | Raft | 43.962 | -111.694 |
| ASP127 | Salmon Falls Creek | Upper Snake | Backpack | 42.049 | -114.741 |
| ASP128 | Sawmill Creek | Upper Snake | Backpack | 44.367 | -113.386 |
| ASP131 | Clover Creek | Upper Snake | Backpack | 43.021 | -115.010 |

| | | | | | |
|---|---|---|---|---|---|
| ASP132 | Big Lost River | Upper Snake | Backpack | 43.574 | -113.258 |

# Appendix E. Targeted Monitoring Site Locations

| Site ID | Stream Name | Location | Latitude | Longitude |
|---|---|---|---|---|
| AST001 | Kootenai River | at US95 bridge | 48.699 | -116.312 |
| AST002 | SF Coeur d'Alene River | at I-90 Business in Mullan | 47.469 | -115.785 |
| AST003 | Priest River | at Peninsula Road | 48.284 | -116.872 |
| AST004 | NF Coeur d'Alene River | at Old River Road | 47.570 | -116.253 |
| AST005 | St. Maries River | at Old County Road | 47.106 | -116.393 |
| AST006 | Palouse River | at State Hwy 9 | 46.915 | -116.741 |
| AST007 | Potlatch River | at State Hwy 3 | 46.857 | -116.400 |
| AST008 | Paradise Creek | at Darby Road | 46.748 | -116.963 |
| AST009 | Snake River | at Southway Bridge | 46.395 | -117.040 |
| AST010 | MF Clearwater River | at State Hwy 13 in Kooskia | 46.147 | -115.979 |
| AST011 | Threemile Creek | at North 7th Street in Grangeville | 45.931 | -116.117 |
| AST012 | NF Payette River | at State Hwy 55 in McCall | 44.912 | -116.119 |
| AST013 | Little Salmon River | at US 95 in New Meadows | 44.973 | -116.295 |
| AST014 | Gold Fork River | at State Hwy 55 | 44.699 | -116.052 |
| AST015 | Weiser River | at Hornet Creek Road | 44.732 | -116.450 |
| AST016 | Mann Creek | at Weiser River Road | 44.242 | -116.867 |
| AST017 | Squaw Creek | at State Hwy 52 | 43.951 | -116.348 |
| AST018 | Deadwood River | at B-L Road crossing | 44.080 | -115.659 |
| AST019 | MF Boise River | at Slide Gulch Road | 43.650 | -115.744 |
| AST020 | Mores Creek | at Steamboat Gulch Road | 43.822 | -115.810 |
| AST021 | Bruneau River | at State Hwy 51 | 42.880 | -115.818 |
| AST022 | Big Wood River | at Warm Springs Road | 43.688 | -114.373 |
| AST023 | Rock Creek | at E3400N near Twin Falls | 42.489 | -114.400 |
| AST024 | Salmon River | at State Hwy 75 | 44.163 | -114.887 |
| AST025 | Salmon River | at US93, in Salmon | 45.177 | -113.898 |
| AST026 | Snake River | at US30, in Burley | 42.545 | -113.762 |
| AST027 | Portneuf River | Center Street in Lava | 42.620 | -112.012 |
| AST028 | Bear River | at US89, near Montpelier | 42.309 | -111.345 |
| AST029 | Blackfoot River | at US91, in Blackfoot | 43.176 | -112.360 |
| AST030 | Bitch Creek | at State Hwy 32 | 43.939 | -111.179 |
| AST031 | Henrys Fork | at US20, near Ashton | 44.111 | -111.447 |
| AST032 | Big Lost River | at Smelter Avenue in Mackay | 43.903 | -113.617 |
| AST033 | EF Salmon River | at State Hwy 75 | 44.267 | -114.326 |
| AST034 | NF Clearwater River | at Cavendish Hwy in Ahsahka | 46.504 | -116.321 |
| AST035 | Snake River | at County Line Road, near IDF | 43.626 | -112.068 |
| AST036 | Camas Creek | at E 2700 N | 44.015 | -112.214 |
| AST037 | Boise River | at Eckert Road | 43.565 | -116.132 |
| AST038 | Salmon River | At US95, Timezone Bridge | 45.445 | -116.311 |
| AST039 | Snake River | at Annex Road | 44.244 | -116.982 |
| AST040 | Snake River | at State Hwy 78 | 42.944 | -115.536 |
| AST041 | Field Blank | various | various | various |