

Standard Operating Procedure: Data Quality Assurance and Quality Control

Arctic Inventory and Monitoring Network

Stream Communities and Ecosystems Monitoring Protocol

Lake Communities and Ecosystems Monitoring Protocol

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The main Narrative for the Protocol for monitoring Stream Communities and Ecosystems for the National Park Service's (NPS) Arctic Inventory and Monitoring Network (ARCN) is available from the NPS ARCN website (<http://science.nature.nps.gov/im/units/arcn>).

SOP: Data Quality Assurance and Quality Control

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Introduction

This standard operating procedure (SOP) defines procedures for quality assurance (QA) and quality control (QC) to be used with the Arctic Network (ARCN) protocols for monitoring Stream Communities and Ecosystems (O'Donnell and Miller 2018a) and Lake Communities and Ecosystems (O'Donnell and Miller 2018b). QA procedures are used to control those unmeasurable components of a project, such as sample at the right place with the right equipment, and using the right techniques. QC data are generated from QC samples to estimate the magnitude of the bias and variability in the processes for obtaining environmental data. QC involves specific tasks undertaken to determine the reliability of field and laboratory data. Together, QA/QC is a substantial part of any monitoring program. The objective of QA/QC is to ensure that the data generated by a project are meaningful, representative, complete, precise, comparable, scientifically defensible, and reasonably free from bias.

Project staff will study this SOP prior to beginning work on the project and follow its procedures in order to conduct the project according to outlined QA/QC procedures. This will ensure consistency and comparability when changes in personnel occur.

The project manager for the Stream Communities and Ecosystems and Lake Communities and Ecosystems vital signs is responsible for the following tasks related to QA/QC:

- Develop, document, and oversee the implementation of standard procedures for field data collection and data handling
- Develop quality assurance and quality control measures for the project
- Contract with an analytical laboratory for analysis of water samples, and ensure lab results meet program needs (e.g., QA/QC procedures, meaningful minimum detection limits for low level strength waters, adequate reproducibility of replicate samples)
- Supervise or perform data entry, verification, and validation
- Summarize and analyze data, and prepare reports
- Serve as the main point of contact concerning data content

The project manager will also work closely with the data manager in the following capacities:

- Complete project documentation in NPSTORET and Aquarius (describing who, what, where, when, why and how of a project)
- Develop data verification, validation, and certification measures for quality assurance
- Coordinate changes to the field data forms and the user interface for project databases
- Identify sensitive information that requires special consideration prior to distribution

- Manage the archival process to ensure regular archival of project documentation, original field data, databases, reports and summaries, and other products from the project

Good Field Practices

Good Field Practices following U. S. Geological Survey (2006):

1. Be aware of and record potential sources of sample contamination at each field site.
2. During water sample collection, wear appropriate disposable, powderless gloves.
3. Use equipment that is constructed of inert materials that will not contaminate the sample or measurement.
4. Use equipment that has been appropriately cleaned according to *SOP: Instrument Calibration for Water Quality Monitoring* and *SOP: Chemical Characterization of Surface Water*.
5. All equipment that is used in the field should be field rinsed. This includes multiparameter sondes, filtering equipment, and sample bottles.
6. Use correct sample-handling procedures. This includes minimizing the number of sample-handling steps and using Clean Hands/Dirty Hands techniques when appropriate.
7. Collect a sufficient number of blanks and other types of quality-control samples.
8. Follow a prescribed sampling order. This is particularly important for water sample collection, as described in *SOP: Chemical Characterization of Surface Water*.

Quality Assurance

Representativeness, comparability, and completeness are three critical components of any set of QA procedures. **Representativeness** is the degree to which data suitably represent (1) the characteristics of a population, (2) parameter variations at a sampling point, (3) a process condition, and/or (4) an environmental condition. Representativeness varies across spatial scales. For instance, at the micro-scale, stream ecosystems vary across stream cross-sections and among channel units. At the macro-scale, stream ecosystems vary across watersheds, biomes, and climate regions. For the Stream Communities and Ecosystems vital sign, the following steps have been taken to ensure the representativeness of samples:

1. We use a stratified sampling approach by sampling replicate watersheds that differ by dominant underlying parent material. Prior work has shown that parent material exerts a significant influence on the chemical composition of arctic stream chemistry (O'Donnell et al. 2016). This approach accounts for representativeness at the macro-scale.
2. As described in *SOP: Field Measurements*, we measure water quality across stream cross-sections using a hand-held multi-parameter sonde to characterize micro-scale variability.

3. All samples are collected during summer base flow conditions during the period of maximum annual thaw depth in the monitoring watersheds (see O'Donnell et al. 2014).

For the Lake Communities and Ecosystems vital sign, the following steps have been taken to ensure the representativeness of samples:

1. All water samples are collected during same time of year (summer) when most arctic lakes are stratified.
2. All samples are collected from the deepest part of the lake, and reflect pelagic zone, not littoral zone conditions.

Another component of QA procedures is to ensure comparability of samples and datasets.

Comparability is a qualitative expression of the confidence that two or more datasets can contribute to a common analysis. Some comparability factors are (1) sample collection, (2) sample preparation, (3) sample analytical methods, and (4) sample detection limits. For the Stream Communities and Ecosystems and Lake Communities and Ecosystems, the following steps have been taken to ensure the comparability of data sets:

1. We collect four basic water quality parameters (temperature, pH, specific conductivity, dissolved oxygen) using a calibrated multi-parameter sonde. These four parameters are collected by all Inventory and Monitoring networks across the NPS nationwide, providing opportunities for cross-site synthesis activities.
2. Chemical analysis of stream and lake water samples are conducted by CCAL at Oregon State University using standard methods per the U. S. Environmental Protection Agency (EPA).
3. Analytical detection limits have been quantified and reported by CCAL (<http://ccal.oregonstate.edu/detection>).

Completeness is another component of QA, and is defined as the amount of valid measurements obtained, expressed as a percentage of the number of measurements that should have been collected. There can be a variety of causes of incompleteness, including sample loss or contamination, error in field collection techniques, errors in laboratory analytical techniques, insufficient amount of sample, or inability to access monitoring sites.

To maximize completeness, the following steps should be taken:

1. Careful sampling procedures are taken to reduce sample contamination and loss. See *SOP: Chemical Characterization of Surface Water*, for examples.
2. Collect sufficient water sample volumes to ensure that there is enough sample volume for all analytical procedures.

3. Account for bad weather days to improve chances of accessing remote monitoring sites and conducting all field measurements and collecting all water samples.
4. Carefully pack samples to reduce chances of sample destruction during transport and shipping.

In addition to representativeness, comparability and completeness, sensitivity is another important component of QA, and is typically determined via laboratory evaluation. **Sensitivity** is defined as the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest. One sensitivity metric is the method detection limit (MDL), which is equal to three times the sample standard deviation of a low-level standard. The minimum level of quantification (ML) is 3.18 times the MDL. Precision is the degree of mutual agreement characteristic of independent measurements as a repeated application of the process under specific conditions. CCAAL report all three of these metrics for each analytical procedure online: <http://ccal.oregonstate.edu/detection>.

Quality Control

Background

The goal of QC samples is to identify, quantify, and document bias and variability in data that result from the collection, processing, shipping, and handling of samples. **Bias** is the systematic error inherent in a method or measurement. Bias can be positive (due to contamination effects) or negative (due to loss/removal). **Variability** is the random error in independent measurements as the result of repeated application of the process under specific conditions. The sources of bias and variability are typically generated from field procedures (i.e. sample collection, processing, shipping), laboratory procedures (processing, analysis), and sample properties.

QC samples are collected to: (1) document the quality of environment data, (2) locate the sources or causes of data-quality problems, (3) assess the comparability of data produced by different methods or procedures, and (4) to understand measurement bias and variability.

Blanks are samples prepared with a special type of water (e.g. deionized water) that is certified to be free of analytes. Blanks are used to test for bias from the introduction of contamination into environmental samples. Replicates are two or more samples that are considered to be essentially identical in composition. Replicates are used to estimate variability for some part of the sample collection and analysis process.

Sources of Contamination

For the Stream Communities and Ecosystems vital sign, there are several sources of sample contamination to be aware of and account for:

- Sampling environment – airborne particulates, precipitation, dust, or soil
- Sample-collection equipment – water samples are collected using a Geotech Pump and tubing

- Sample-processing equipment – water samples are filtered using high-capacity disposable capsule filters and are stored in a range of different sample bottle types
- Transport and shipping – samples are stored in coolers in the field, transported from the field to town by helicopter or fixed-wing aircraft, and shipped to the lab by Fed Ex aircraft.
- Storage – samples are stored in either a refrigerator (e.g. DOC or DIC) or freezer (e.g. nutrients)
- Personnel – dirty hands, sweat, etc.

Field blank collection

To determine if water samples are contaminated as a result of field activities and exposure, a field blank is collected. Field blanks are collected and processed at the field site in same manner as the collection of field samples. Field blanks should be collected within the same inference space as the stream or lake samples. Inference space is the location in space and time within which the results of the experiment are valid. Thus, for the Stream Communities and Ecosystems vital sign, field blanks should be collected from each of the five dominant parent-material classes. Field blanks don't identify the source of the contamination. To identify the source of the contamination, a suite of topical QC samples can be collected. If it appears that the sampling process is resulting in a biased result from contamination, refer to methods for collecting topical QC samples to identify the source of the problem (U. S. Geological Survey 2006).

To collect a field blank, follow these steps:

1. Rinse equipment with appropriate blank water three times.
2. For inorganic samples, use inorganic-grade blank water (IBW).
3. Collect the IBW blank sample using the sample methods as described in *SOP: Chemical Characterization of Stream Water*.
4. For organic samples (e.g. dissolved organic carbon, DOC), use pesticide-grade water (PBW).
5. Rinse equipment at least three times with PBW.
6. Then, collect the PBW blank for analysis of organic compounds.
7. Field blanks should be collected routinely to account for possible variation in sampling in processing, including:
 - a. Sampling from different site types (stream vs. lake) or site conditions (raining vs. sunny).
 - b. Working out of different villages (Kotzebue vs. Nome vs. Bettles).
 - c. Sampling with different equipment (e.g. filter types, new tubing, etc.)

Field Replicates

Concurrent replicates are two or more samples collected simultaneously or at approximately the same time. Concurrent replicates are collected from a subset of monitoring sites to estimate variability introduced from collection, processing, and shipping of environmental samples. They also help to characterize inherent variability in an aquatic ecosystem across a short distance in space or time. Field replicates should be collected at a minimum of 10% of monitoring sites during each field season. Additional field replicates can be taken to examine spatial variation within an aquatic ecosystem (e.g. upstream vs. downstream sites, riffle vs. pool, main channel vs. slough, etc.)

Laboratory QA/QC

Most water samples for the Stream Communities and Ecosystems monitoring protocol are analyzed at the Cooperative Chemical Analytical Laboratory (CCAL) at Oregon State University (<http://ccal.oregonstate.edu/>). CCAL has developed a Quality Assurance Plan (QAP) that describes protocols and procedures used in the laboratory, so that results conform to surface water chemistry criteria as prescribed by the Environmental Protection Agency (EPA). The QAP can be accessed online via the CCAL webpage:

<http://ccal.oregonstate.edu/sites/ccal/files/pdf/QAP%20Rev%203%202013.pdf>. Here, we briefly describe some of the main QA/QC procedures used by CCAL.

Acid-washing of sample bottles

CCAL provides ARCN personnel with sample cleaned and acid-washed samples bottles for collection of streamwater samples. Sample bottles are washed in a 0.5 M hydrochloric acid (HCl) bath and then repeatedly rinsed with deionized water. The project manager can request a specific number and type of bottles for streamwater sampling. Similar acid-washing and rinsing steps are conducted for beakers and bottles associated with laboratory analytical procedures.

Sample Custody

All samples should be submitted to the laboratory as soon as possible following collection. Samples should either be refrigerated or frozen, following *SOP: Chemical Characterization of Surface Water*. When submitting samples to CCAL, all samples should be appropriately labeled and a completed sample log sheet should be completed. The sample log sheet should describe requested sample analyses.

Once samples are received by CCAL, samples are entered into a tracking system, which tracks sample condition upon receipt, number of samples, and date of receipt. Prior to analysis, samples are thawed and logged into an electronic database. Samples are given a project code (e.g. ANJO, or “Arctic Network Jon O’Donnell”) and numbered consecutively. Samples are either stored in a cold room (at 4°C) or a freezer (-20°C) until analyzed. When ready for analysis, samples are thawed and analyzed as soon as possible.

Calibration and Analytical Procedures

For each analytical procedure, CCAL has a specific SOP that they follow (<http://ccal.oregonstate.edu/sops>). Prior to conducting analyses, lab staff calibrate balances and

pipettes. Calibration standards are prepared for each constituent using National Institute of Standards and Technology (NIST) standards. Instruments are calibrated at the beginning of each sample run. An analytical check standard is run approximately every 10 samples to insure accuracy and precision, and check standards must be within 10% of theoretical value. Method detection limits have been determined for each analytical procedure.

Internal Laboratory Quality Control Checks

Internal calibration QC checks at CCAL include the following:

- Calibration correlation should be greater than 0.995 between expected and measured values for NIST traceable standards for each chemical constituent.
- Analytical drift is monitored using check standards.
- Sample duplicates on 10% of samples are used to estimate instrument precision.
- To estimate accuracy, CCAL participates in the U.S. Geological Survey Standard Reference Surface Water test program.
- Blanks are used to monitor carry-over between runs.

Data Verification

Verification is the examination of data to ensure that they are free of transcription, coding, or other such errors, and that all documentation is correct and complete. Verification steps can be conducted in either Microsoft Excel or following import into NPStoret. For the Stream Communities and Ecosystems and the Lake Communities and Ecosystems vital signs, the following verification procedures are employed:

1. Confirm that SOPs and analytical methods were actually employed.
2. For any calculations (e.g., summary statistics in reporting), project manager performs a double check to ensure that calculations are correct.
3. Confirm that data present in formal laboratory reports is consistent with field or laboratory notes.
4. Assess field and laboratory uncertainty using field and laboratory replicates, respectively.

Data Review

The data review process involves an examination of the laboratory results to ensure that reported values are reasonable. For the Stream Communities and Ecosystems and Lake Communities and Ecosystems vital signs, the following data review procedures should be followed:

1. In a Microsoft Excel spreadsheet, check to see if values or concentrations exceed maximum observed values for these. Refer to recent NPS Data Series Reports for stream

and rivers (O'Donnell et al. 2015a) and large lakes (O'Donnell et al. 2015b) to prescribe maximum concentrations.

2. Identify data outliers using either a box-plot approach or by generating histograms.
3. Compare among data values by plotting concentration vs time.

Data Validation

Data validation is an analyte-specific process to determine the analytical quality of a specific data set. These steps should be conducted in NPStoret. Validation steps include:

1. Review laboratory reports from CCAL for consistency and completeness.
2. Assign or review data qualification codes.
3. Evaluate analytical performance:
 - A. Calculate relative percent difference (RPD) between field duplicates following equation (1), and
 - B. Calculate RPD between laboratory duplicates, following equation (1):

$$RPD = \frac{100(\text{Sample} - \text{Duplicate})}{\text{Mean}} \quad (1)$$

where *Sample* is the concentration of the sample, *Duplicate* is the concentration of the duplicate, and *Mean* is the average of the Sample and Duplicate concentrations.

In addition to characterizing variability through duplicates, it is important to assess bias or contamination by analyzing field blank data. For detailed methods on how to analyze blank data, see work by Mueller et al. (2015). The results of the analytical performance should be reported in any products, including annual reports, technical reports, or peer-reviewed journal articles.

Data Certification

Data certification is the confirmation procedures conducted to ensure that all planned QA/QC tasks have been implemented according to either a Quality Assurance Plan (QAP) or a Data Quality Standards document. Certification implies that the dataset is of analytical quality.

Discharge

Stream discharge data used by this protocol are certified by the USGS and available from the NWIS database. No specific ARCN certification procedures are required.

Discrete Water Quality Data

Discrete water quality data is stored and processed in the I&M program's NPStoret database. Data certification is dependent on passing ARCN and WRD's stringent data quality checks and implied by

acceptance of data by WRD into STORET. The NPStoret database will be uploaded annually to the IRMA Data Store according to the schedule of deliverables.

Continuous *In Situ* Water Quality Measurements

The ARCN Streams and Lakes monitoring programs will follow WRD's guidance and standard operating procedures for data certification. Specifically, the Aquarius continuous water quality monitoring database allows users to tag records 'Public', 'NPS-Only' and 'Restricted'. Records passing quality control and data verification checks authorized by the project leader will be tagged 'Public' indicating they are of analytical quality, and thus "certified". Such records then become publicly available to the Aquarius Web Portal (<https://irma.nps.gov/aqwebportal/>).

Discrete Field Samplings

Field data measurement records are by default tagged 'Provisional' in the streams monitoring database until such time that they have been fully processed and verified (NPS 2016). The project leader then reviews data quality and authorizes some or all the records to be marked 'Certified', documented and published to the IRMA Data Store. The ARCN Streams and Lakes monitoring programs will follow ARCN's standard model for generating and publishing a certified dataset as described in ARCN/CAKN DMSOP-1 (Miller 2017).

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