RECLAMATION

Managing Water in the West

2021 Quality Assurance Plan
USBR-CPN Regional Water and Soil Laboratory
Boise, Idaho

U.S Department of the Interior
Bureau of Reclamation
Columbia-Pacific Northwest Region
Boise, Idaho

Signature KRISTINA LAWCYNELL Digitally signed by KRISTINA LAWCYNELL Date: 2021.05.03 14:31:22 -06'00' Date _____

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Reviewer/Editor

MISSION OF THE BUREAU OF RECLAMATION

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

INTRODUCTION

The US Bureau of Reclamation's (USBR/BOR) Pacific Northwest (PN) Regional Soil and Water Laboratory (Water Lab) provides sample collection and field and laboratory analyses for water and soil quality studies throughout the region. The Laboratory provides water quality information related to operation, maintenance, and resource planning issues at Reclamation project facilities. It also assists States, Tribes, watershed councils, and irrigation districts in their watershed planning and restoration efforts. Laboratory data is used for activities such as Total Maximum Daily Load (TMDL) development, trend analysis, wetland design, drain water characterization, groundwater quality management, facility compliance monitoring, reservoir nutrient budgets, and special investigations.

It is the business practice of the Laboratory to provide valid, reliable, and accurate data by adhering to a sound quality assurance (QA) program. The degree of quality control (QC) practices applied to specific sample sets will depend on the requirements set to meet the data quality objectives. This QA plan describes the minimum QC practices, procedures, and methods required in the Laboratory.

ORGANIZATION AND RESPONSIBILITY

Laboratory personnel consist of a lab manager, three chemists and one to six field and laboratory technicians. The number of technicians varies with the workload. Figure 1 shows the overall organizational structure and QA responsibilities followed by a short resume of each staff member in Table 1.

Full-time employees are required to accurately perform all major Laboratory activities. Repetition results in greater efficiency and increased awareness of QC problems, therefore, each employee is generally responsible for certain measurement systems and Laboratory activities. The responsibilities of the quality assurance officer (QAO) are as follows:

- Involve each analyst in QC activities through U.S. Geological Survey (USGS) and commercial reference materials, duplicates, spikes, and blanks.
- Provide for performance audits.
- Collect and assess data for precision and accuracy.
- Prepare QA reports.
- Prepare the QA plan and revisions.
- Identify equipment needs, maintenance, and training to meet QA requirements.
- Assist staff in other divisions and offices in preparation of sampling and analysis work plans to assure that data quality objectives are met.

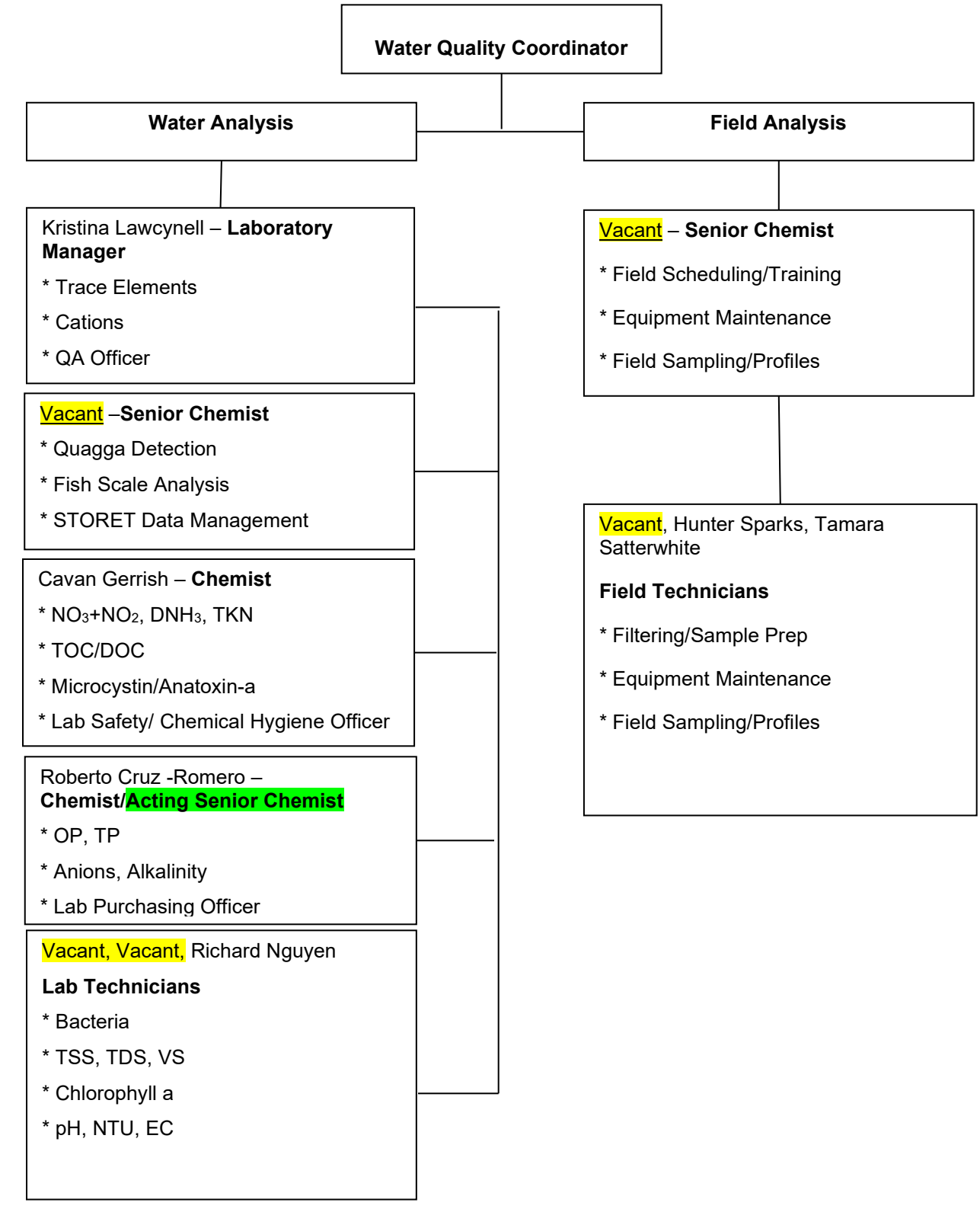

Figure 1. Organizational structure of the PN Regional Laboratory.

Table 1. Qualifications of Laboratory personnel.

Staff	Position	Experience	Education
Vacant	Water Quality Coordinator		
Kristina Lawcynell	Laboratory Manager	18 years	BS Biochemistry and Chemistry, Idaho State University 2003
Cavan Gerrish	Chemist	7 years	BS Chemistry, The College of Idaho 2014
Roberto Cruz Romero	Chemist	5 years	BS Chemistry, Boise State University 2016
Vacant	Technician		
Vacant	Technician		
Richard Nguyen	Technician	2 year	Currently enrolled Boise State University
Vacant	Field Technician		
Hunter Sparks	Field Technician	1 Year	Currently enrolled Boise State University
Tamara Satterwhite	Field Technician	1 Year	Currently enrolled Boise State University

LABORATORY FACILITIES AND EQUIPMENT

The Laboratory is located at 300 East Garrison Road in Boise, Idaho. The facility houses both the Laboratory and a portion of the PN Regional Hydromet office (Figure 2). The Hydromet areas are independent of the Laboratory and Hydromet employees do not have access to the Laboratory areas except for the rest rooms.

The Laboratory is equipped with three fume hoods and three atomic absorption hoods. There are 10 chemical resistant sinks in the lab and each is plumbed with hot and cold water, deionized (DI) water, and an aspirator. All of the Laboratory benches are of steel construction with chemical resistant tops. Each bench is supplied with compressed air, natural gas, and cup sink. One bench is equipped with a water bath regulated at 20^{o}C. There is a separate storage room for compressed gasses and an individual closet room for acids. The file room in the Laboratory is used for long-term storage of raw data, reference material, and files, and is keyed separately to provide security.

The DI water supply system, located off the back of the garage in a separate room, can supply up to 47 gallons per hour of high purity DI water. The two garage areas provide storage for the field boat and mobile laboratory. The major instruments and equipment owned and operated by the Laboratory are listed in Table 2. All instruments and equipment are serviced and calibrated annually, if required.

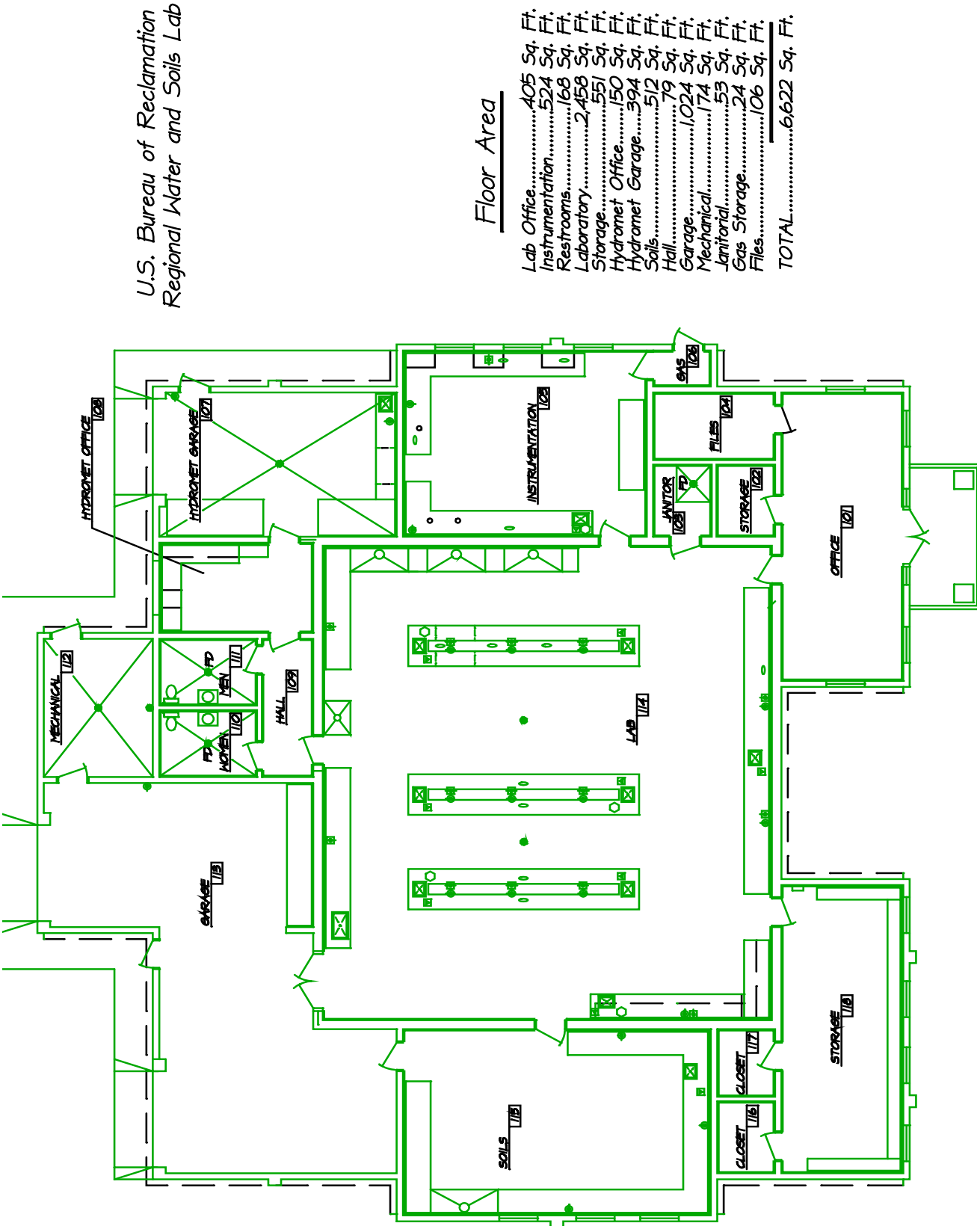

Figure 2. PN Regional Laboratory layout.

Table 2. **Major Laboratory equipment and instruments.**

Equipment	Manufacturer
Segmented Flow Analysis System (5)	Seal Analytical AA3
Atomic Absorption Spectrophotometer Furnace/Flame	Perkin Elmer Analyst 5100
Atomic Absorption Spectrophotometer Furnace/Flame	Perkin Elmer Analyst 800
Carbon Analyzer	O-I Analytical Aurora Model 1088
Balances	Mettler AB54, AB104, PC4000, BD202, PG503, PB3002, NewClassic MF
Turbidimeters	HACH 2100N
Autoclaves	Tuttnauner 2540M (2), Ritter M11
Bacteria Incubators	Precision, Boekel, Barnstead, Hach
BOD Incubator	Precision
Refrigerators	Kelvinator Scientific, LAB RepCo (2), Magic Chef (2), K2 Scientific
UV-VIS Spectrophotometer	Thermo Electron Corporation Genesys 6
Conductivity Meters	Various
pH/Specific Ion Meters	Various
Mobile Lab	Ram 2015
Boats	18ft Duckworth, 18 ft Hewes Craft
Canoe	Coleman
Multi-parameter Field Probe	HydroLab DS-5/Surveyor, YSI 556MPS
Lake-Bottom Sediment Sampler	Wildco
Stream Flow Measurement Device	Marsh/McBirney
Submersible Recording Thermograph	Onset
Programmable Auto Sampler	ISCO
Dissolved Gas Meter	Common Sensing
Microwave Digestion System	CEM Corporation
Centrifuge	Fisher Scientific
ICP-OES	ThermoFisher iCap 7000 Series
Ion Chromatograph	Dionex ICS-1100
Autotitrator T50	Mettler Toledo
Water bath (2)	ThermoFisher Sci, Precision
UV-Vis Multiplate reader	Abraxis

SAMPLING PROCEDURES

When Laboratory personnel are responsible for sample collection, the sampling procedures outlined in the *Handbook for Sampling and Sample Preservation of Water and Wastewater* (EPA 1982) will be followed. Some projects will have specific sampling plans; therefore, the project sampling plan will take precedence over any other sampling protocols. Variations in sampling sites, procedures, or frequencies must be approved by the project coordinator or QA officer.

Sampling protocols for use in river surface waters and reserviors are shown in figures 3 and 4 below.

Preservatives and container types used for sampling are as recommended by the Environmental Protection Agency (EPA) methods which are summarized in Table 3.

Table **3**. Recommended preservation methods and holding times for wastewater. **(EPA 1983b)**

Parameter	**Preservation Method**	**Container**	**Maximum Holding Time**
Alkalinity	Store at 4°C	P,G	14 days
Ammonia	$H2SO_4$ to pH<2, Store at 4°C	P,G	28 days
Anatoxin-a	Store at 4°C, Freeze at -20 °C	Amber PETG, Amber Glass	7 days refrigerated; 28 days frozen
Bacteria	Store at 4°C	P, G	30 hours
Chloride	None	P,G	28 days
Chlorophyll a	at 4°C, on filter, in airtight, dark	P,G	3 weeks
Dissolved Oxygen	None	G	Analyze immediately
Fluoride	Store at 4°C	P	28 days
Hardness	HNO_3 to pH<2	P,G	6 months
Microcystin	Store at 4°C, Freeze at -20 °C	Amber PETG, Amber Glass	7 days refrigerated; 28 days frozen
Nitrate + Nitrite	$H2SO_4$ to pH<2, Store at 4°C,	P,G	28 days
Ortho-phosphate	Store at 4°C	P,G	48 hours
pH	None	P,G	Analyze immediately

Parameter	Preservation Method	Container	Maximum Holding Time
Phosphorus, total	H_2SO_4 to pH<2, Store at 4°C	P,G	28 days
Quagga	At least 25 % Ethanol	P	Indefinite
Residue, filterable and non-filterable	Store at 4°C	P,G	7 days
Silica	HNO_3 to pH<2	P	6 months
Specific Conductance	Store at 4°C	P,G	28 days
Sulfate	Store at 4°C	P,G	28 days
Total Kjeldahl Nitrogen	H_2SO_4 to pH<2, Store at 4°C	P,G	28 days
Total Metals	HNO_3 to pH<2	P,G	6 months
Total Organic Carbon	H_2SO_4 to pH<2, Store at 4°C	G	28 days
Turbidity	Store at 4°C	P,G	48 hours
Notes: P = HDPE or LDPE Plastic; G = Glass,			

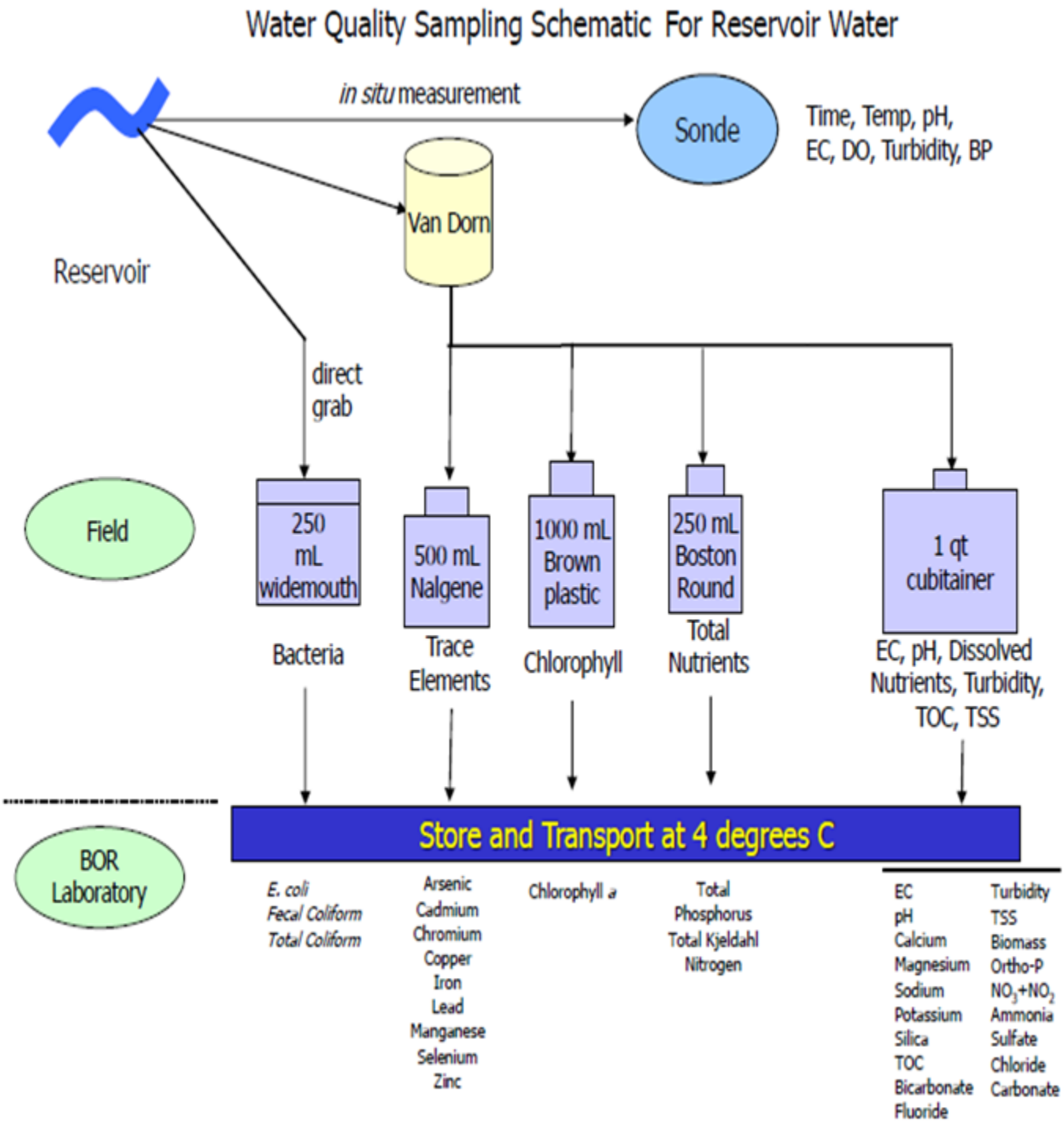

Figure 3. Reservoir Water Sampling Schematic

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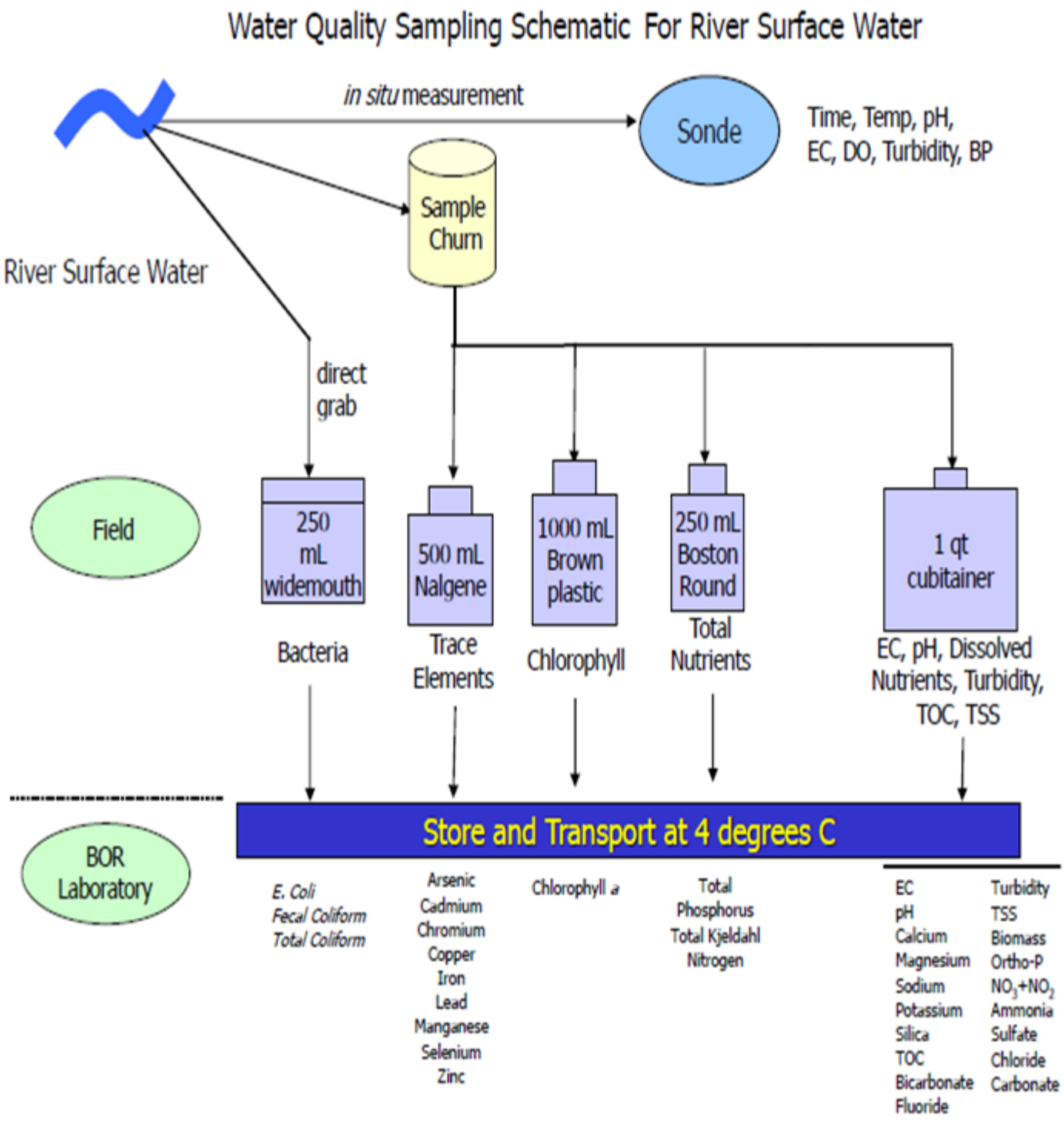

Figure 4. River Surface Water Sampling Schematic

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CHAIN OF CUSTODY/DATA FLOW

When samples are received in the Laboratory, the employee who logs them in becomes the sample custodian. The sample custodian will sign the *chain of custody* section of the field data sheet that accompanies the samples. The field data sheet should identify the sampler, the transporter, and the sample custodian. The custodian will be responsible for the samples until their disposal. If incoming samples have no field sheet or *chain of custody* form, the custodian will fill out a blank substitute field sheet and record information from the sample containers on that form.

Samples received in the Laboratory are logged into the Element Laboratory Information Management System (LIMS) by the sample custodian. Element assigns each chain of custody a work order number and each sample on the workorder a sequential number in the format of:

YYMM(Number of work orders in the current month 001-999)-(sample # on workorder 01-99)

For example the 12th sample of the 23rd work order in 2019 in the month of January would be 1901023-12.

Information put into Element includes the EPA's national water quality data storage and retrieval system (STORET) site code, an alternate code and/or the site location description, date received, date sampled, time sampled, all field information, analyses requested, and notes/comments about sample conditions and field recording errors. The sample custodian is responsible for assigning analysis during log-in that may be required but was not automatically assigned by Element

After samples are logged into Element, initial information relating to the samples or the sample batch is entered.. All notes and data put into Element are stored in the database and associated with its respective sample. Changes to the database are backed up daily and a full back-up is performed weekly by an external drive back-up system.

The Element database is continually growing and changing. Changes, additions, and deletions are noted by the program and are logged in an audit trail log. The audit trail log includes information about who is making the change, date of the change, the original value or note, the new value or note, and may include the reason for the change.

When an analysis is completed, the results are entered into Element onto a batch created by the analyst. Calculations for some analyses may be performed by bench/batch sheet templates built outside of Element. When the results are entered and double checked by the testing analyst, sample status is updated to analyzed and the raw data sheet is signed by the testing analyst. The batch is then reviewed by a non testing analyst, the raw data sheet is signed as reviewed by the non-testing analyst and the sample status in Element is updated to reviewed.

Completed samples are cross checked by Element (Table 4). Element flags samples during data entry/review referencing corrections that need to be made before the data can be released to a client or to EPA's STORET. After all analyses and checks are completed for a sample batch, a final report can be generated from the Element.

Table **4**. Element cross checks.

Check	**Criteria**
EC vs TDS	EC X .64 . TDS
Anion/Cation	90 – 110%
TP≥DP≥OP	Total phosphorus should always be greater than or equal to dissolved phosphorous which should always be greater than or equal to ortho phosphorus
TKN≥NH_4	TKN should always be greater than or equal to ammonia
SS vs NTU	The suspended solids and NTU are somewhat correlated
pH vs Carbonates	If the field pH is over 8.3 then there should be a carbonate value
Total Coliform > Fecal Coliform > *E.coli*	Number of total coliform colonies per 100 mL should always be greater than the number of fecal coliform colonies per 100 mL and the number of fecal coliform colonies per 100 mL should always be greater than the number of *E. coli* colonies per 100 mL. Occasionally, this criteria will not be met due to the limitations of method. Any excessive inequalities will be taken as an indication of a problem that need to be addressed as outlined in Figure 7.

Samples are logged out and discarded one month after QC criteria have been met on all the required analyses, the final reports sent, and the STORET files created. The samples are recorded in the sample log-out book and then discarded. After one month from the report date all raw and acid-fixed samples are disposed down a Laboratory sink connected to a neutralizing tank. The containers are recycled. Raw data reports are discarded after 4 years.

Once data has gone through the final report stage in Element, a STORET transfer file can be manually staged by an Element user. The STORET transfer file is a comma delimited ASCII file that can be electronically transferred to the STORET database. A STORET retrieval of all data is requested in January for data submitted in the previous year. This data is reviewed and edited before uploading.

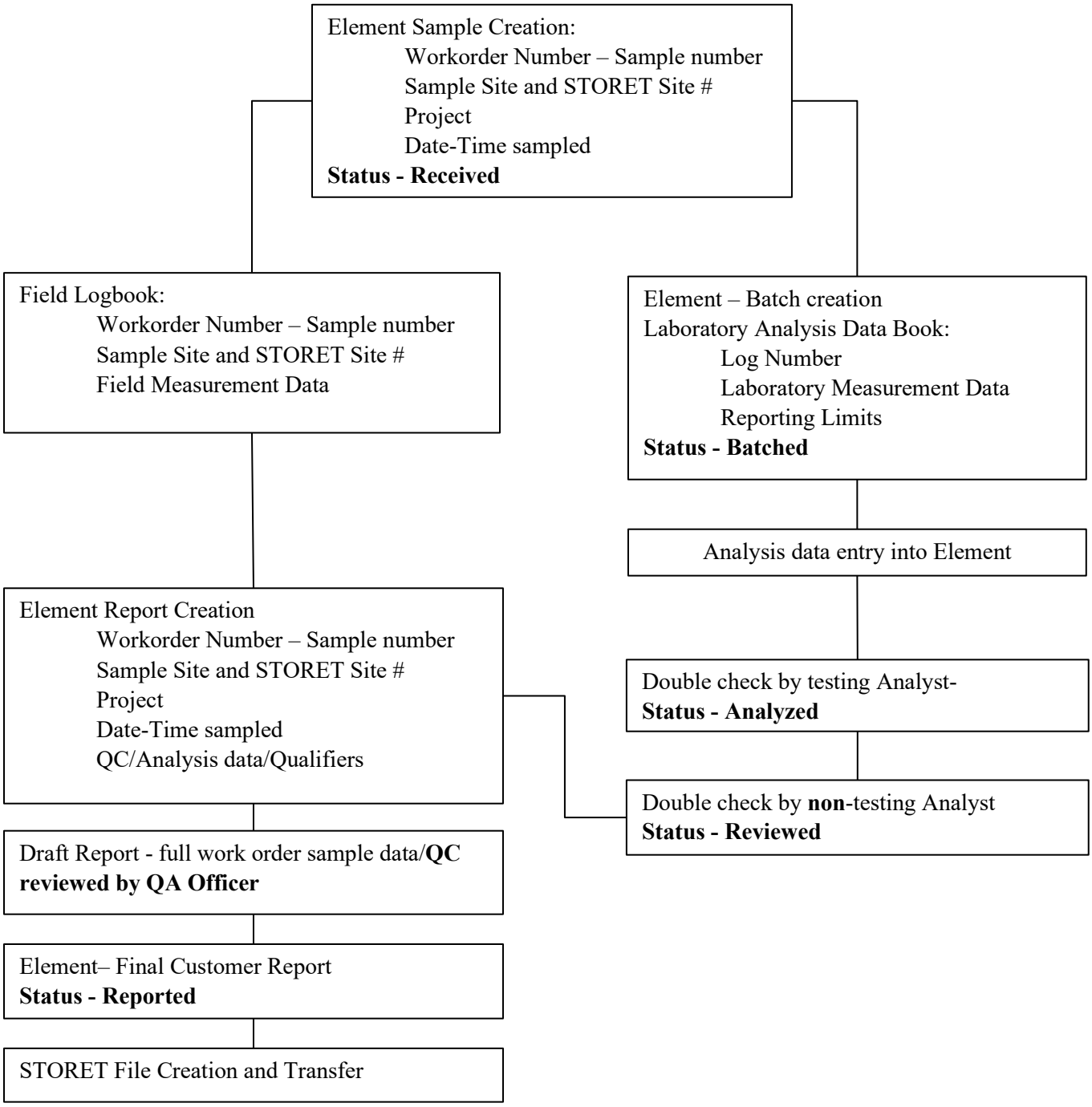

Figure 5. Data flow and reporting scheme.

DETECTION LIMITS

The method detection limit (MDL) is the minimum analyte concentration measurable by the analytical instrument which is quantifiable at a 99 percent confidence interval. The MDL is calculated using the previous 24 months of data for both low level spikes and method blanks and ideally 1 low level spike is ran monthly within the same run containing a calibration curve and sample QC packages. 2 samples per quarter is the stated requirement However, if MDL samples cannot be ran monthly or quarterly due to lack of client samples or instrument needs, 7 samples per 24 months is the bare minimum. Method blanks are used from regular sample testing. The spike MDL is calculated as follows:

$$MDL_S = t_{(n-1,\ 1-\alpha=0.99)} S_s$$ where:

MDL$_s$ = the method detection limit based on spiked samples

t (n-1, 1-α = 0.99) = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom (i.e 12 samples = 11 degrees of freedom). See **Figure 6** for $t_{.99}$ values.

S_s = sample standard deviation of the replicate spiked sample analyses.

The method blank MDL is calculated as follows:

$$MDL_b = \overline{X} + t_{(n-1,1-\alpha=0.99)} S_b$$ where:

MDL$_b$ = the MDL based on method blanks

$\overline{X}$ = mean of the method blank results (use zero in place of the mean if the mean is negative).

t (n-1, 1-α = 0.99) = the Student's t-value appropriate for the single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom (i.e 12 samples = 11 degrees of freedom).. See **Figure 6** for $t_{.99}$ values. If number of method blanks or low level spikes exceeds listed t-values on right, use microsoft excel and input the formula =TINV(0.02, # of samples – 1) to calculate a t-value and round the result to the 3rd decimal place.

cum. prob	$t_{.99}$
one-tail	0.01
two-tails	0.02
df	
1	31.82
2	6.965
3	4.541
4	3.747
5	3.365
6	3.143
7	2.998
8	2.896
9	2.821
10	2.764
11	2.718
12	2.681
13	2.650
14	2.624
15	2.602
16	2.583
17	2.567
18	2.552
19	2.539
20	2.528
21	2.518
22	2.508
23	2.500
24	2.492
25	2.485
26	2.479
27	2.473
28	2.467
29	2.462
30	2.457

Figure 6. t_{99} value table

S_b = sample standard deviation of the replicate method blank sample analyses.

The verified MDL is the greater of the MDL_s or MDL_b. MDLs are determined on an annual basis for each parameter tested that produces a continous distribution of results (i.e presence/absence methods or microbiological results involving colony counting do not require an MDL) and are recorded in the raw data books. If the newly verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of method blanks exceed the existing MDL, then the existing MDL can be left unchanged from the previous year.

The procedures for determining MDLs are adapted from the Code of Federal Regulations Appendix B of Title 40, Part 136, Section 3 and from EPA 821-R-16-006 Definition and Procedure for the Determiniation of the Method Detection Limit, Revision 2.

The limit of quantitation (LOQ) or minimum reporting level (MRL) is always greater than the method detection limit. LOQ summaries are recorded in the front of each raw data book. The LOQ for water quality parameters tested for in the Laboratory are listed in

Table 5.

Table 5. Analytical procedures and limit of quantitation detection limits.

Parameters	Limit of Quantitation[1]	Units	STORET Code Number	EPA[2] Method Number	GS[3] Method Number	SM[4] Method Number
Alkalinity	5	mg/L as $CaCO_3$	00410			2320 B
Ammonia, Dissolved - Colorimetric	0.02	mg/L as N	00608	350.1		
Anions:						
Chloride	0.5	mg/L	00940	300.0[5]		
Fluoride	0.1	mg/L	00950	300.0[5]		
Sulfate	0.5	mg/L	00946	300.0[5]		
Bacteria:						
Total Coliform	1	ct/100 mL	31503			9222 B
Fecal Coliform	1	ct/100 mL	31616			9222 D
E. coli	1	ct/100 mL	31627			9213 D
Barometric pressure	1	mm Hg	00025			
Bicarbonate – Titration	1	mg/L as $CaCO_3$	00440			2320 B

Parameters	Limit of Quantitation[1]	Units	STORET Code Number	EPA[2] Method Number	GS[3] Method Number	SM[4] Method Number
Biochemical oxygen demand – 2 day	0.5	mg/L	00304			5210 B
Biochemical oxygen demand – 5 day	0.5	mg/L	00310			5210 B
Biomass	1	g/m^2	00573		B-3520-85	
Carbonate – Titration	1	mg/L as $CaCO_3$	00445			2320 B
Cations – Direct Method:						
Calcium	0.2	mg/L	00915	200.7		
Magnesium	0.2	mg/L	00925	200.7		
Potassium	0.2	mg/L	00935	200.7		
Sodium	0.2	mg/L	00930	200.7		
Chlorophyll-a	1[6]	mg/m^3	32210			10200H
Conductivity, Field	2	µmho/cm	00094			2510 B
Conductivity, Laboratory	2	µmho/cm	00095			2510 B
Cyanotoxins - ELISA						
Microcystin/Nodularins	0.24	ug/L (ppb)				
Anatoxin-a (VFDF)	0.3	ug/L (ppb)				
Dissolved oxygen	0.1	mg/L	00300	360.1		
Dissolved solids by summation		mg/L	70301		I-1751-85	
Nitrate + Nitrite	0.01	mg/L as N	00631	353.2		
Organic carbon, Dissolved	0.2	mg/L	00681			5310 C
Organic carbon, Total	0.2	mg/L	00680			5310 C
Pheophytin-a	1[6]	mg/m^3	32218			10200H
pH, Field	0.05	SU[7]	00400			4500 H+ B
pH, Laboratory	0.1	SU[7]	00403			4500 H+ B

Parameters	Limit of Quantitation[1]	Units	STORET Code Number	EPA[2] Method Number	GS[3] Method Number	SM[4] Method Number
Phosphorus, Ortho	0.003	mg/L as P	00671	365.1		
Phosphorus, Total	0.01	mg/L as P	00665	365.1		
Quagga	1	veliger				10200 G
Silica	0.4	mg/L as SiO_2	00955	200.7	I-2700-85	
Streamflow		cfs[8]	00061			
Temperature	0.1	°C	00010	170.1		
Total nonfilterable residue (TSS)	1	mg/L	00530		I-3765-85	
Total filterable residue (180°C) (TDS)	10	mg/L	70300			2540 C
Total kjeldahl nitrogen	0.05	mg/L as N	00625	351.2[9]		
Trace Elements – Direct Method						Digestion 3030K[4]
Iron	10	µg/L	01045	200.7		
Manganese	5	µg/L	01055	200.7		
Zinc	10	µg/L	01092	200.7		
Trace Elements – Direct Method						
Arsenic	2	µg/L	01002	200.7		
Cadmium	2	µg/L	01027	200.7		
Chromium	2	µg/L	01034	200.7		
Copper	2	µg/L	01045	200.7		
Lead	2	µg/L	01051	200.7		
Selenium	5	µg/L	01147	200.7		
Turbidity	0.5	NTU[10]	00076	180.1		
Volatile Solids	1	mg/L	00520	160.4		

[1] Limit of Quantitation is always greater than the method detection limit and verified annually. Also called MRL
[2] *Methods for Chemical Analysis of Water and Wastes* (EPA 1983a)
[3] *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments* (USGS 1989)
[4] *Standard Methods for Examination of Water and Wastewater* (APHA 1998)
[5] *Methods for Chemical Analysis of Water and Wastes* (EPA 1983a) [6]Based

Parameters	Limit of Quantitation[1]	Units	STORET Code Number	EPA[2] Method Number	GS[3] Method Number	SM[4] Method Number

on volume filtered; 1-1000 mL filtered [7]Standard units
[8] Cubic feet per second
[9] A 100 mL micro kjeldahl system is used in place of a block digestion system
[10] Nephelometric turbidity units

QUALITY CONTROL OBJECTIVES

Holding Times

Maximum allowable sample holding times are listed in **Table 3** of the "Sampling Procedure" section on page 8-9. These guidelines are adapted by the Laboratory as recommended by the EPA (EPA 1983b). Samples that exceed holding times before analysis are qualified in Element with a "run past hold time qualifier".

Samples collected by Laboratory personnel will adhere to the recommended preservation methods and container types in **Table 3**. For any errors made in preservation or container types, the Laboratory supervisor will consult with the project manager before proceeding with the affected analyses.

Working standards and SRM's generally expire and are discarded **1 calender year** from the laboratory preperation date (child standards expire **1 calender year** from preperation date **NOT** when the parent standard expires). Exceptions are made for source vials from ERA which are discarded **after 4 years,** stock solutions (first solution made from source material e.g. dry chemical) are discarded **after 2 years**. Any manufacturer recommended changes to standard expiration dates (or reagents) take precedent over internally assigned numbers. If a solution no longer measures within 10% of the calculated value, it can be reran once. If it fails again, it is discarded along with any data from that run.

Precision

Precision refers to the relative agreement between duplicate determinations and serves as a record of repeatability of an analytical procedure. Replicate determinations will be made from subsamples taken in the Laboratory. The replicate sample should be analyzed as the last sample in a set of 10 samples. Precision is expressed as Relative Percent Difference (RPD). For samples that are suspected of being less than the reporting limit, duplicate spike samples should be used to guarantee a quantified value for the RPD calculation.

$$RPD = \frac{A - B}{\frac{A + B}{2}} x100$$

Where: A = Concentration value for sample
B = Concentration value for replicate

The Laboratory precision objectives are listed in Table 6 and include:

- For concentration ranges greater than 20 times the reporting limit the RPD must be 10 percent or less.
- For concentration ranges greater than 5 times the reporting limit, but less than 20 times the reporting limit the RPD must be 20 percent or less.
- For concentration ranges that are less than 5 times the reporting limit, the absolute difference must not exceed ±1 reporting limit. Replicates in this range are qualified with a "Difference (= or <) MRL" qualifier.
- Field duplicates are generally considered to be less precise than laboratory QC duplicates and therefore the RPD must be 20 percent or less at all concentration ranges greater that 5 times the reporting limit.

If replicate samples are suspected of being less than the reporting limit, then a different sample should be replicated instead.

Table 6. PN Regional Laboratory precision objectives.

QC Objective	Frequency (per number of samples)	Acceptance
Precision	10	> 5 MRL – 20 MRL 20% or less > 20 MRL 10% or less < 5 MRL ± 1 MRL
Accuracy	10	See Table 5 for specific parameters
Reference	1 per run	90-110% of true value
Blank	20	< 1 MRL
Calibration Checks: Calibration Blank Calibration Verification	10/end	 < 1 MRL 90 – 110% of standard value
Notes: LOQ = Limit of Quantitation > Method Detection Limit		

If precision objectives are not met for a sample set, the data for that particular sample set is rejected and corrective action taken as illustrated in **Figure** . All precision results are circled or highlighted in the raw data books.

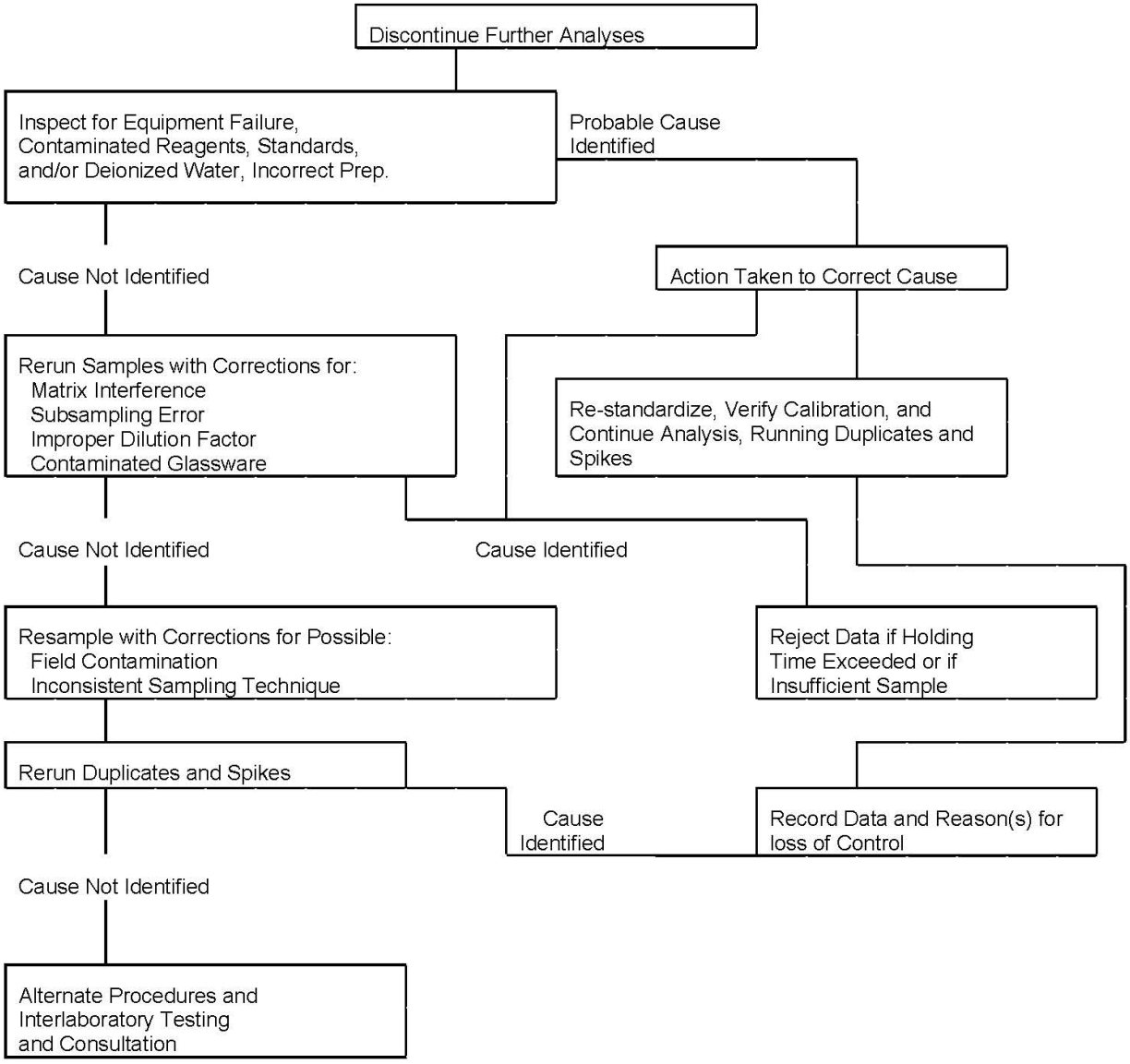

Figure 7. Flow chart for outlier corrective action.

Accuracy

Accuracy refers to the closeness of analytical results to the true parameter concentrations of spiked samples and is expressed as a Percent Recovery (PR).

$$PR = \frac{R - S}{A} x100$$

Where: R = amount of constituent recovered in a spiked sample
S = amount of constituent in the sample
A = amount of constituent added as spike

The analysis of one spiked sample in 10 is completed to assist in evaluating accuracy. When available, past sample data is used to adjust spike concentrations to approximate sample concentrations except in cases where measurements approach quantitation limits. Spike volumes should be as small as possible relative to the sample aliquot, but not so small that they cannot be dispensed accurately. Spiked samples are picked at random.

Laboratory accuracy objectives (Table **7**) are based on past Laboratory performance and regulatory limits. Control charts with enhanced precision objectives are available based on blank spike recovery data. If accuracy objectives are not met for a sample set, the data is rejected and corrective action taken as shown in Figure . Overall accuracy is assessed by the evaluation of solutions with known concentrations as further discussed in "Reference Sample" section (page18). All accuracy results are circled or highlighted in the raw data books.

Table 7. Accuracy objectives.

Parameter	Accuracy Objective (PR)
Ammonia	90-110%
Anions	90-110%
Arsenic – ICP-OES	70-130%
Cadmium - ICP-OES	70-130%
Cations	70-130%
Chromium - ICP-OES	70-130%
Copper - ICP-OES	70-130%
Iron - ICP-OES	70-130%
Lead - ICP-OES	70-130%
Manganese - ICP-OES	70-130%
Nitrate + Nitrite	90-110%
Ortho Phosphate	90-110%
Selenium – ICP-OES	70-130%
Silica	70-130%
Total Kjeldahl Nitrogen	90-110%
Total Organic Carbon	90-110%
Total Phosphate	90-110%
Zinc - ICP-OES	70-130%
Cyanotoxins	60-140%

Blanks

Blanks are used to measure the effects of reagents, sample preparation, digestion, and contamination on analyte concentrations in the sample.

When Laboratory personnel are responsible for sample collection, one field blank is collected for every 20 samples or per sample set. The field blank consist of laboratory-pure water and is collected in the same type of container as the samples. The field blank is treated as a sample and goes through the same preparatory steps as the samples for each requested analysis.

When performing analyses, Laboratory method blanks are introduced to the sample set (or a minimum of 1 in 20 samples) at the appropriate preparation step. If a sample needs to be filtered, a method blank is also filtered to prove no contamination was introduced during the filtering process. All digestion processes include a digestion/method blank.

Blanks should not exceed the analysis detection limit.

Reference Sample

Reference samples are used to check the ability of the analytical technique to accurately measure the analyte of interest concentrations. Reference samples are either ampouled concentrations or prepared natural waters. Commonly used reference samples are from the U.S. Geological Survey (USGS), Environmental Resource Associates (ERA). Reference samples are treated as a sample and should be the first sample analyzed after the initial calibration and initial calibration verficiation. At least one reference sample is run per sample batch.

Criteria for acceptance of reference sample results are based on the percent recovery. % recovery is calculated for standard references using the equation below.

$$\%\ Recovery\ Std.ref. = \frac{(\text{Std ref result})}{(\text{Calculated value})} * 100$$

Standard references must have **90% - 110%** recovery to be valid (or meeting manufacturer specific recoveries).

Chemical Ionic Balance

Because water is an electrically neutral system, the sum of the milliequivalents of the cations in solution must equal the sum of the milliequivalents of the anions. The major cations include calcium, magnesium, sodium, and potassium. The major anions are carbonate, bicarbonate, chloride, sulfate, and nitrate. When all major cations and anions are determined in a sample, the

anion/cation percentage is the predominant quality control requirement for these constituents. The anion/cation percentage is calculated by the formula:

$$\frac{Anions(me/L)}{Cations(me/L)} x100$$

The calculated value for the anion/cation percentage must fall between 90 and 110 percent. Samples that are outside the upper or lower control limits are considered out of control and corrective action is taken. Samples with unusually high fluoride, nitrate, or ammonia levels will sometimes contribute significantly to the anion/cation percentage and are added to their respective constituents.

Calibration

To assure proper instrument calibrations, the following Laboratory practices must be part of the standard operating procedure.

- Use good analytical technique in preparation of reagents and standards.
- Prepare standards from certified primary standards or from reagent grade chemicals.
- Compare older standards or previously analyzed Standard Reference Materials to freshly prepared standards and provide correction for any discrepancies.
- Check standards frequently.
- Incorporate standard reference sample following initial calibration.
- Adhere closely to manufacturers' instrument instructions.

Analytical instruments are calibrated at the beginning of an analysis run using a calibration blank and standards of known concentrations of the analyte. At least two standards and a blank are used for segmented flow, flow injection, and nonlinear atomic absorption flame analyses when the concentrations are below 1 part per million (ppm). When the concentrations are between 1 ppm and 3 ppm, then at least three standards and a blank are used. If a wide concentration range is used, then at least five standards and a blank are necessary.

After ten samples, the instrument calibration is checked with a low and high standard. If the instrument has drifted more than an amount equal to the detection limit on the low end or 5 percent on the high end, recalibration and analysis is conducted for all samples analyzed since the last good calibration.

Furnace atomic absorption analyses are calibrated with duplicate injections. Duplicate injections have a Relative Standard Deviation of 10 percent or better before sample analysis begins. Linear atomic absorption flame analysis is calibrated according to the manufacturer's recommendations and check standards are used immediately after a calibration to verify linearity.

For analyses where the standards do not require the same pretreatment as the samples, then calibration accuracy must be verified by an independent calibration verification standard. The verification standard must be analyzed immediately after standardization and the verification standard must be within 90 to 110 percent of the true value. Calibrations that do not meet verification requirements are considered out of control and corrective action must be taken.

Specific ion meters are calibrated by using a range of three standards at the beginning of each batch.

Analytical balances used for quantitative work such as standard preparation are calibrated before each use with 3 independent weights traceable to the National Institute of Science and Technology. Balances are also calibrated **annually** by an external company.

Pipettes are calibrated **quarterly** via gravimetric water calibration based on manufacturer tolerances. If pipettes are consistently out of calibration, either decommissioned or sent to the manufacturer for service.

The conductivity meter is calibrated before each use with DI water, a low standard, and a high standard within the expected working range of samples.

Lab pH meters are calibrated with a minimum 2-point calibration with a pH range not greater than 3. Wider sample ranges require a 3-point calibration and all samples must fall within the calibration range.

Instruments for field measurements of dissolved oxygen (DO) and pH are calibrated at each sampling station. DO meters are air calibrated according to manufacturer’s instructions. The pH meters are calibrated according to manufacturer’s instructions with a minimum 2-point calibration with a maximum pH range of 3. Samples must fall within the calibration range. For stations that require multiple readings, calibrations are checked after the last reading.

Thermometers are calibrated **annually** against a NIST digital thermometer or upon initial receipt and when their calibration certificate expires.

Baromters are periodically checked against a spare instrument and the mercury barometer.

The Hydrolab field measurement instrument is calibrated according to the manufacturer's recommendations. The calibration is verified at the conclusion of data collection by taking

readings of standards of known concentrations. QC objectives for recalibration are the same as for Laboratory requirements.

DATA REVIEW AND CORRECTIVE ACTION

Data is reviewed following the Data Flow and Reporting Scheme (

Figure 5, page 14). Upon completion, field sheets are reviewed and signed in approval by the QA officer. The QA officer is responsible for random checks to verify that field data is correctly entered into Element and abnormalities are noted by way of exception reports. Additionally, the QA officer is responsible for checking at least 10 to 20 percent of the data on a random basis to insure that information from the raw data books are accurately entered into Element. A new employee's raw data is reviewed on a more intense basis until competence is assured.

For most parameter measurements, QC objectives that are out of control are identified and immediately corrected by the analyst. Because of the variability between procedures, it is difficult to define a corrective action suitable to cover all cases. However, if any of the QC objectives have not been met for a sample set, then the guidelines shown in Figure 7 are used for troubleshooting. The analyst will consult with the supervisor when the situation cannot be effectively remedied through normal corrective action procedures. Corrective actions made by Laboratory analysts are documented in the raw data books. Corrections related to instrument mainteance are also noted in the instrument maintenance log (i.e. changing dirty pump tubes affecting baseline drift).

Data will also be subjected to peer review. Analysts are assigned parameters to review that are not parameters they normally would analyze. The analyst reviews the assigned raw data books and signs for each batch of samples analyzed if the data meets the QC objectives.

PREVENTIVE MAINTENANCE

Preventive maintenance includes proactive actions designed to prevent equipment (or parts) failure during use (i.e., equipment cleaning, lubricating, reconditioning, adjustments, testing).

The main objective of the preventive maintenance program is to increase the system reliability; thereby decreasing downtime and increasing data completeness.

Each major piece of equipment has a separate maintenance notebook for documenting problems, repairs, date of service, and the employee responsible for service. Maintenance routines are shown in Table 8.

Table 8. Equipment maintenance routines.

Equipment	Maintenance Routine
Electrodes	Replenish the electrolyte in reference electrodes as needed. Change membrane and filling solution on NH_3 electrode once every 2 weeks. Change membrane and filling solution on dissolved oxygen meter probes monthly or if response time is slow. Clean EC meter electrode after each use with deionized water
Balances	Remove instrument weights after each use. Clean pan and external surfaces. Schedule certified maintenance and traceable calibration by service technician annually
Nephelometer	Remove, clean, and readjust the lamp semiannually. Inspect and discard worn cuvettes before use
Burets	Flush with titrant before use and with deionized water immediately after use. Cover to protect from dust.
TKN digestion assembly	Replace tubing every 6 months and clean manifold after each use.
Autoclave	Clean after each use and add DI water as needed. Follow manufacturer's recommendations for maintenance
Bacteria vacuum pump	Clean filter and check oil level quarterly.
Lab countertops	Clean all surfaces with moistened paper towels weekly. Replace bench paper as needed.
Boat	Schedule preventive maintenance and safety check annually with a qualified dealer.
Mobile lab	Follow manufacturer's maintenance schedule.
Supplies	Keep a running inventory of routinely used chemicals. A "shopping list" is conveniently located in the Laboratory that notes item, quantity, and date required. Anytime an expendable item is used, the analyst will assess the quantity on hand and reorder as necessary. Keep readily available spare parts such as electrodes, filling solutions, filters, instrument lamps, and pump tubes.
Inductively Coupled Plasma- Optical Emmision Sprectroscopy	Follow manufacturer's recommended maintenance. Software alerts operator when maintenance needs to be completed.
Seal Analytical AA3	Follow manufacturer's maintenance recommendation. Pump tubes should be changed monthly or more frequently under heavy sample loads. Lubricate pump according to manufacturers' instructions. Flush system after daily run for 15 minutes with deionized water, leaving water in the system. Clean platen surface weekly with alcohol and lint-free wipes. Wash pots are emptied and swabed with alcohol monthly.

Equipment	Maintenance Routine
DI water system	Perform and document service on the DI water treatment system as recommended by the installer (**Table** 9**)**. Complete operating instructions are on file in the lab. Conductivity measurements for DI water are taken weekly at a DI faucet to monitor for any degradation in water quality. Conductivity measurements should be less than 0.5 mho/cm or corrective action should be taken
Dionex ICS-1100	Follow manufacturer's recommended maintenance.
Mettler Titrator	Follow manufacturer's recommended maintenance. Schedule with Mettler once a year. Replace electrode filling solution every 6 months.

Table **9**. DI system maintenance.

Replacement Item	Frequency	Notes
Demineralizer	6 months	
Carbon filter	6 months	
Prefilter	Semi-annually	
Submicron filter	Bi-annually	
Air filter	Annually	
UV light	As needed	
RO cartridge	12 – 15 months	Changed when efficiency is less than 95 percent
Softener salt	As needed	Usually about one bag per month

PROCEDURES

Standard operating procedures (SOP) for the approved method are maintained in the PN Regional Laboratory Manual (PN002). The SOP's are edited as procedures and methods are revised.

Only approved methods described in the *Methods of Chemical Analysis of Water and Wastes* (EPA 1983a), *Standard Methods for Examination of Water and Wastewater* (APHA 1998), and *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments* (USGS 1989) will be followed.

QUALITY CONTROL DATA

Quality control data is entered into Element along with data from the raw data books on a continuous basis. The Element database is maintained on the file server in the Laboratory file room. Only Laboratory personnel have access rights to the information on the file server. QC data entered in Element includes precision, accuracy, reference deviations, and anion/cation balance. Suspected QC problems are analyzed anytime using Element, control charts, and statistical summaries. It is the responsibility of the analyst to be aware of bias trends of the analytical results and to meet the QC objectives set forth in the QA plan.

QA reports are prepared by the QA officer on a case-by-case basis to assist clients and managers with specific QC information and issues including:

- Assessments of accuracy and precision.
- Results of performance and system audits.
- Significant QA problems, corrective actions, plans, and recommendations.
- Other QA information requested by Reclamation management or cooperating agencies.

QA reports are available to clients upon request.

TRAINING

New Laboratory personnel are briefed on the organizational structure, key personnel, overall Laboratory functions, various types of tests performed, materials tested, and water quality projects being performed.

Trainees are instructed on general Laboratory techniques including safety, proper use, care and cleaning of glassware, care and use of balances and other equipment, sample custody and sequence for sample handling, and data processing.

Trainees will review the lab copy of the QA plan and Laboratory Manual (WL002) and if necessary, they will receive their own copy. They are required to review the QA plan and Laboratory procedures for parameter measurements and performance requirements. After familiarization with a written procedure, the trainee is given a reference sample to perform a specified test under the guidance of an experienced technician. The test is repeated until the results consistently recover 90-110% of reference material. Small sample batches containing a duplicate, spike, and a blind sample are tested. The supervisor reviews data from each batch with the trainee to identify and resolve any problems with accuracy or precision. The trainee is required to follow the guidelines outlined for QC in the QA plan, and Laboratory results are closely monitored until

the trainee achieves proficiency in a procedure. After the analyst is deemed competent in a procedure, it is recorded in the training file.

Continual training for all Laboratory personnel includes:

- Communications with universities, state, and Federal agencies, and commercial laboratories
- Seminars
- Literature review of current books and periodicals
- Workshops sponsored by manufacturers of laboratory equipment

EXTERNAL PERFORMANCE AUDITS

Laboratory personnel participate in the semi-annual USGS Analytical Evaluation Program Standard reference water samples which are analyzed for major constituents and nutrients. Deficiencies are identified by the supervisor and corrected by the analyst.

Laboratory personnel also participate in an annual Performance Evaluation Study conducted by Environmental Resource Associates. Deficiencies are identified by the supervisor and corrected by the analyst.

The Laboratory is certified for most parameters by Washington State Department of Ecology (WDOE).

LABORATORY SYSTEM EVALUATION

Laboratory system evaluations are on-site Laboratory inspections and reviews of the quality control system. These evaluations are used to identify problems and correct deficiencies in operational program elements. System reviews may be specific to a project or general to include all of the Laboratory operations. Past evaluations were performed by USGS, Reclamation, and WDOE. Evaluations are currently performed once every 3 years by WDOE.

SAFETY

Each Laboratory employee is issued and required to follow the current years *PN Regional Water and Soil Laboratory Chemical Hygiene Plan* (WL003). For specific policies and requirements, refer to this manual.

REFERENCES

Parenthetical Reference	Bibliographic Citation
APHA 1998	American Public Health Association (APHA). 1998. Standard Methods for Examination of Water and Wastewater. APHA-AWWA-WPCF. 20th Edition.
EPA 1983a	Environmental Protection Agency (EPA). 1983a. Methods of Chemical Analysis of Water and Wastes. EPA-600/4-79-020. March.
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Element LIMS	Promium. 2018. Element version 6 User guide. Promium LLC, 3350 Monte Villa Parkway, Suite 220, Bothell, WA 98021.
USBR 2007a	U.S. Bureau of Reclamation. 2007a. *PN Regional Laboratory Manual*. Revised edition. Pacific Northwest Region. Boise, Idaho. July.
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