

WATER QUALITY MONITORING PROJECT PLAN  
FOR THE  
DEPARTMENT OF ENVIRONMENTAL QUALITY  
WATER MONITORING AND ASSESSMENT PROGRAM

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QUALITY ASSURANCE PROJECT PLAN  
FOR THE  
DEPARTMENT OF ENVIRONMENTAL QUALITY  
WATER MONITORING AND ASSESSMENT PROGRAM

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## A.4 PROJECT/ TASK ORGANIZATION

Figures 1 and 2 depict the organizational structures of the Virginia Department of Environmental Quality (VADEQ) and Division of Consolidated Laboratory Services (DCLS) for the Water Monitoring and Assessment (WMA) program. The associated responsibilities for VADEQ and DCLS personnel for the program are as follows:

### DEQ Regional Field Staff:

- Perform all field activities including field measurements, observations and sampling in accordance with the most recently approved Quality Assurance Project Plan (QAPP) and Standard Operating Procedures (SOPs).
- Notify immediate supervisors and WMA QA Coordinator of any issues encountered.

### DEQ Regional Program Planners:

- Manage the day to day operations of the Ambient Water Monitoring Project in the regions.
- Supervise regional conductance of the project in accordance with this project plan.
- Coordinate routine WMA program activities.
- Provide input and implement Regional Program Manager's recommendations regarding program development, implementation and overall program management.

### DEQ Regional Program Managers:

- Make recommendations for corrective action as requested by regional personnel.
- Assure that activities in the regions meet the requirements of the program as outlined in this project plan.
- Provide recommendations regarding the development, implementation and overall management of the program.

### DEQ Laboratory Liaison:

- Coordinates program activities between the Regional Office staff and DCLS including sample collection scheduling based on laboratory capabilities.

### DEQ Quality Assurance Coordinator:

- Revises and updates the existing Quality Management Plan, Quality Assurance Project Plan and Standard Operating Procedures Manual to ensure that approved practices and procedures are available for use by program personnel.
- Coordinates QA activities among contracted laboratories to ensure quality in analytical results and data validity. When necessary monitors laboratory performance using a blind check sample program and performs inspections and recommends corrective actions when necessary.
- Presents training in field sampling and measurements; conducts/ coordinates agency audits of the program; reports to management on the quality assurance

aspects of the program and where appropriate, makes recommendations for corrective action.

DEQ Monitoring Coordinator:

- Implements the project plan and manages the Commonwealth's water quality monitoring strategy through the formal establishment of program policy, objectives, priorities and methodologies.
- Participates in specialized intensive scientific studies in water quality, seeking improved technologies and methodologies in the detection and quantification of environmental pollutants.

DEQ WMA Data Manager:

- Responsible for the overall strategy and functioning of the monitoring program.
- Assists in the duties of supporting staff including QA Coordinator and Monitoring Coordinator and by facilitating cooperation of planning and program managers at Regional Offices throughout the state.
- Performs all aspects of data management, including tracking, compilation and review of data entry. Identify and corrects errors and ensures automated uploads of data to database are completed as scheduled.

DEQ Non-Agency Data Liaison

- Main point of contact between DEQ and citizen volunteer and other non-DEQ monitoring programs.
- Conducts training and audits of field monitoring activities from non-DEQ monitoring programs.

DEQ WMA Program Managers:

- Assure that activities in the regions meet the requirements of the program as defined in this project plan.
- Provide recommendations regarding the development, implementation and overall management of the program.

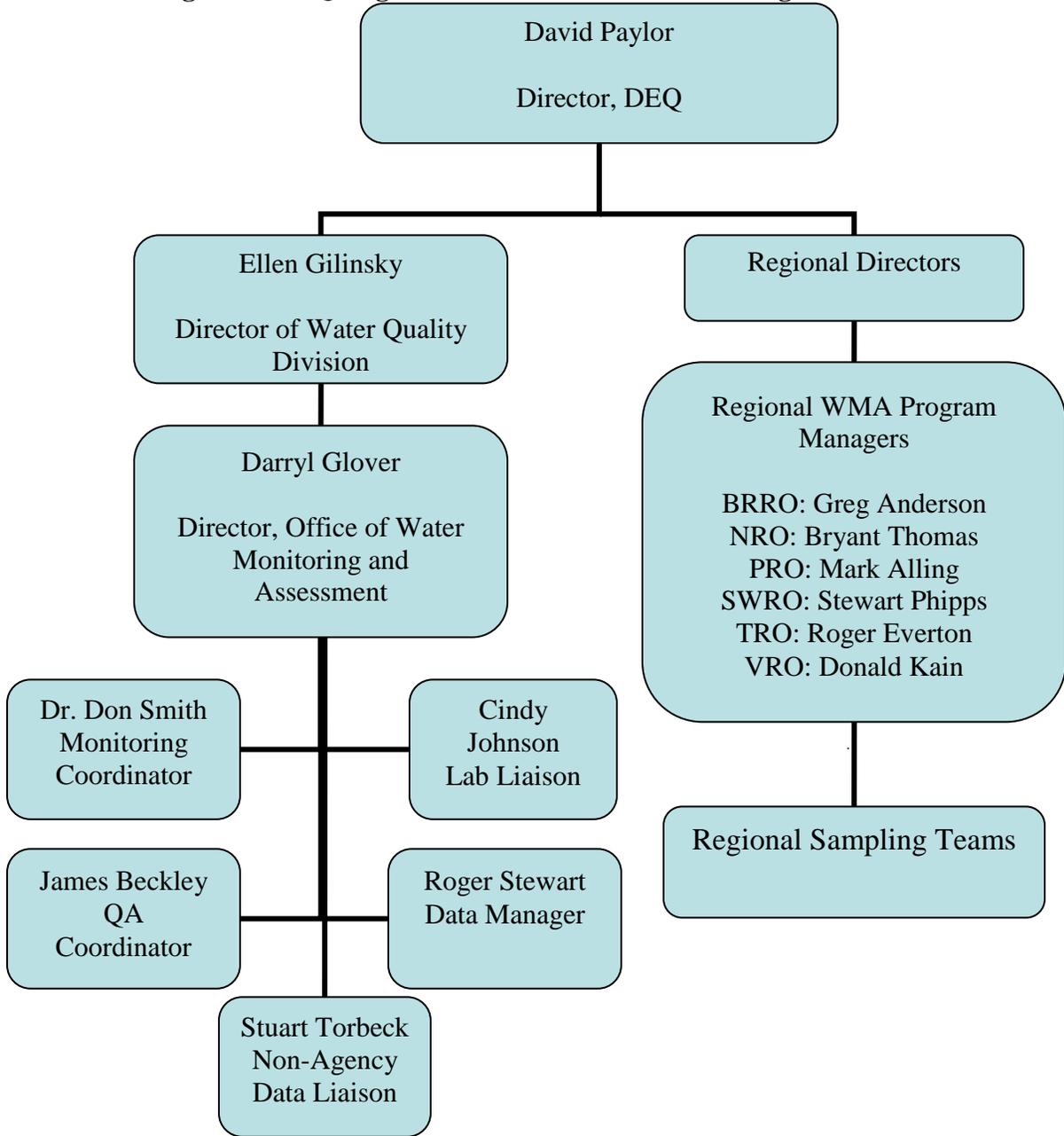
DCLS Laboratory Managers:

- Manage the laboratory departments performing analyses on samples taken as part of the WMA program
- Responsible for oversight of all analytical activities and to ensure all activities are performed during laboratory analysis are in accordance with the DCLS Quality Manual.

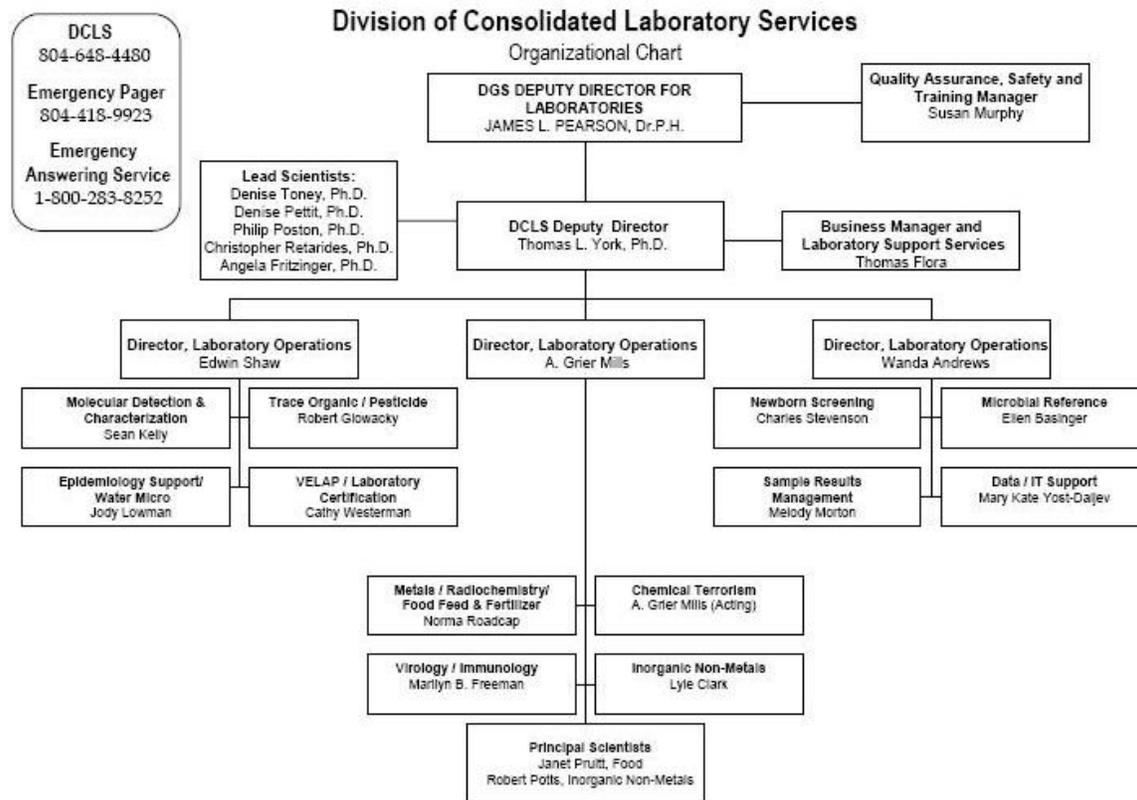
DCLS QA Officer:

- Responsible for establishing, implementing and coordinating a comprehensive QA/QC program for analyses and ensuring that the analytical operations producing environmental data are of sufficient quality to meet or exceed requirements for informed decision making.

Figure 1. DEQ Organizational Chart for WMA Program Network



**Figure 2. DCLS Organizational Chart**



REVISED: 3/10/2010

## A.5 PROBLEM DEFINITION/BACKGROUND

Funding agreements between Virginia and the Environmental Protection Agency (EPA) require Virginia to monitor the Commonwealth’s waters and report the results to the EPA to support the goals of the Clean Water Act.

In Virginia, the state legislature passed the “Water Quality Monitoring, Information and Restoration Act” (“WQMIRA- VAC Chapter 3.1 of Title 62.1 Article 4.1 62.1-44.19:4 through 62.1-44.19:8 – March 18, 1997) requiring an evaluation of the Commonwealth’s environmental protection program. WQMIRA ushered in a new era for VADEQ’s water quality monitoring efforts by identifying specific areas needing improvements to meet the growing needs of the commonwealth. Areas targeted for improvement included providing consistency in monitoring methods, the evaluation of water quality trends, the distribution and abundance of toxics, sampling frequency, and the expansion of geographic coverage to include all state waters. Additionally intergovernmental agreements are consistently demanding more of our monitoring programs, including the development of Total Maximum Daily Loads (TMDLs) for those stream segments identified as impaired in biennial 303(d) reports. These changes, along with

WQMIRA, mark a shift in emphasis that extends beyond monitoring to include the characterization and resolution of problems found during the monitoring efforts.

The ultimate goal of the WMA program is to provide accurate data that will permit the evaluation, restoration and maintenance of the quality of the Commonwealth's waters at a level that provides for multiple uses as prescribed by Federal and State laws.

In order to achieve this goal, and to satisfy scientific, legislative, and aesthetic requirements related to the quality of the Commonwealth's water resources, VADEQ has established a series of specific objectives to identify and define the diverse functions of WMA program. Many of these specific objectives are directly related to the following five general objectives set forth in the Clean Water Act.

1. Determination of water quality standards attainment (section 305(b)).
2. Identification of impaired waters (section 303(d)).
3. Identification of causes and sources of water quality problems (section 305(b) and 303(d)).
4. Support for implementation of water management programs (sections 303, 314, 319, 402 etc.)
5. Support for the evaluation of program effectiveness (sections 303, 402, 314, 319 etc.)

To attain the overall goal of the agency's WMA program and the general objectives of the Clean Water Act, below are specific objectives of the WMA program:

1. Provide accurate, representative data for water quality characterization and assessment of all surface water statewide.
2. Establish consistent statewide parameter selection and monitoring techniques, in order to ensure data reliability and comparability throughout the agency.
3. Assure that frequency of sampling and the total number of observations collected are sufficient to provide adequate data using statistically based and scientifically defensible assessment procedures.
4. Wherever possible and as available resources permit, assure flow rates are determined simultaneously with the collection of water quality data.
5. Monitor, according to a plan and schedule, all substances that are discharged into Commonwealth waters subject to Virginia Water Quality Standards or otherwise necessary to determine water quality conditions.
6. Continually evaluate the overall success of Commonwealth's water quality monitoring and management efforts.
7. Provide adequate data and analytical procedures for short, medium and long-term statistical evaluations of water quality variation and trends within identifiable, geographically or hydrologically defined water bodies.

## A.6 PROJECT/TASK DESCRIPTION AND SCHEDULE

### A.6.1 Work to Be Performed

Currently, there are 456 active watershed stations and 378 trend stations across the state in the monitoring network. Most of the stations in the non-coastal regions are accessed by land via bridge crossings or other public access points. Estuaries and other large waterbodies are monitored by boat.

The WMA program focuses primarily on the chemical, physical, and bacterial pathogen characteristics of the water column. The indicators are primarily selected from those chemicals that have current state water quality standards and can be cost-effectively analyzed. Additional indicators are also included that may not have specific associated standards but are considered useful for interpretation of other measurements such as identifying long-term trends.

A basic suite of core indicators is measured at all stations. Additional indicators may be added depending on site specific concerns such as stream classification, discharge types and historical or suspected issues. Additional field observations of weather conditions are also recorded at all site visits.

All the core indicators are listed in Table 1.

**Table 1. Core Water Quality Monitoring Indicators**

Watershed Station	Trend Station
Temperature, pH, specific conductance, salinity, dissolved oxygen, ammonia, total nitrogen, total phosphorus, total suspended solids, E. coli or Enterococcus	Temperature, pH, specific conductance, salinity, dissolved oxygen, ammonia, nitrite + nitrate, total nitrogen, total phosphorous, total suspended solids, total solids, E. coli or Enterococcus, chlorophyll a

### A.6.2 Work Schedule:

The trend program is geared towards collection of long-term data and is therefore a continuous program of indeterminate duration. The watershed program consists of sampling all of Virginia's watersheds on a 2 year rotational basis, such that when one watershed is completed another is started. Data stations are typically visited bimonthly year-round for collection of field measurement and analytical samples. Collection for the watershed program will also continue indefinitely. Designated monitoring field staff in each Regional Office performs sampling for both programs. When staff shortages and/or position vacancies occur, trained volunteers and summer interns may conduct the sampling.

Individual field staff determines their specific daily sampling schedule. Flexibility in scheduling site visits is needed to allow field staff to balance their workloads, reschedule for inclement weather, and allow for equipment availability. Field staff makes every effort to complete all work as scheduled.

The WMA program is an on-going program requiring sample collection and analysis throughout the year. Data produced for the program are reviewed quarterly for QA/QC purposes to ensure data are valid when assessed for 305B designations every 2 years.

Because the WMA budget is dependent upon available state resources, VADEQ has set up a priority scale for the various water quality monitoring efforts conducted by the regions. Trend stations are considered priority 1 indicating the sites will be monitored even in times of limiting resources to prevent the possibility of data gaps.

Watershed stations are designated as priority 2 allowing limited flexibility in the sampling protocol. Under priority 2 conditions, the frequency of sample collection may not change, but the number of sampling sites on a given watershed may decrease during times of limited resources. If the number of sites is reduced, the number and positioning of the remaining sites sampled must still be able to adequately describe ambient conditions in the watershed.

## **A7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA**

### ***A.7.1 Data Quality Objectives***

Data Quality Objectives (DQOs) are qualitative and quantitative statements that specify the quality of data required to support specific WMA decisions. DQOs also specify the level of that uncertainty that a decision maker is willing to accept in results derived from monitoring data are used in a regulatory or programmatic decision, such as establishing analytical method requirements, establishing sampling protocols and revision or development of industry standards.

The WMA program, using existing performance information on the methods and procedures contained in this document, developed the DQOs defined in this section. Because DQOs are established through an iterative process, these values may be adjusted by the WMA QA Coordinator based on continual evaluation of performance data generated during this program.

The main objective of this document is to provide monitoring data of known and documented quality. These data will be used in the establishment of baseline water quality conditions based on the following criteria:

1. Analysis of trends in water quality and comparison with water quality standards.
2. Evaluation of the effectiveness of the implementation of water quality controls
3. Performance of water quality assessments in the biennial water quality inventory report (the 305(b) report) to EPA
4. Establishment of stream segment ranking (303(d) listing)
5. Providing data and guidance to managers and modelers during the restoration phase.

The DQOs for this program are provided in Table 2.

The quality of data generated by various sampling activities can be expressed in terms of comparability, representativeness, precision, bias, and completeness using the following criteria.

➤ **Comparability**

Comparability refers to the extent to which the data generated by this program is comparable to other studies conducted in the past or from other areas. To ensure comparability, VADEQ requires the use of standardized sampling and analytical methods, uniform units of reporting, and standardized site selection procedures. The comparability of laboratory data produced for the DEQ WMA is by DCLS and other contracted laboratories to use standardized methods, where possible, including EPA approved analytical methods, Standard Methods, USGS Methods, or documented modifications thereof which provide equal or better results. These methods have specified units in which the results are to be reported.

➤ **Representativeness**

The representativeness of the data is mainly dependent on locations of sampling sites and the use of sampling procedures that produce results representative of the true conditions when the sampling occurred. The goal for meeting total representation of the site is limited by the types and number of potential sampling points and media being sampled as well as the potential funding required for meeting complete representativeness.

It is well known fact that water flowing past a given location on land is constantly changing due to multiple factors including response to inflow, tidal cycle, weather, etc. Wherever possible and applicable, sampling schedules and collection methodologies will be designed with respect to frequency and sampling locations to maximize the representativeness of each site. However, in the collection of bed sediment samples the sampling design focuses on the collection of fine, recently deposited sediment, which can introduce a built-in bias that may not be thoroughly representative of the typical bed sediment within a particular sampling site.

➤ **Precision and Bias**

The precision and bias of data are determined by particular actions and methods used by the analytical laboratory and field staff. The precision of data is a measure of the reproducibility of the measurement when the analysis is repeated. It is usually reported in Relative Percent Difference (RPD). The bias of an analysis is a measure of how much of a constituent actually present is determined. It is typically measured, by adding a known amount of a constituent to a sample and determining how much of the added constituent (spike) is then measured. This spike analysis is reported as Percent Recovery. The acceptable RPD and acceptable percent recoveries are dependent on many factors including: analytical method used, laboratory used, media of sample and constituent being measured.

➤ **Completeness**

The completeness of data is the relationship of how much data are available for use compared to the total available data collected before any conclusion is reached. Ideally, 100% of the data should be available. However, there is always the possibility of data becoming unavailable due to laboratory or equipment error, insufficient sample volume, or samples broken during shipment. In addition, unexpected situations may arise where field

conditions do not allow for 100% data completeness. Due to these unforeseen possibilities, WMA considers 90% data completeness sufficient to generate meaningful data.

➤ **Sensitivity**

Sensitivity is defined as the ability of the method or instrument to discriminate between measurement responses. For this program, WMA and state laboratory personnel employ the most sensitive method and instruments possible to analyze the samples.

➤ **Method Detection Limits (MDL)**

In general, an MDL is the smallest amount of analyte that can be detected above signal noise and are within specified confidence levels. MDLs are calculated in the laboratory by analyzing a minimum of seven low level standard solutions using the procedures in the Federal Register, 40 CFR Part 136 Appendix B (Revision 1.11).

**Table 2. Data Quality Objectives for Non-metal Analyses and Field Parameters**

Analyte	Matrix	Units	MDL*	Accuracy Goal	Precision Goal
Temperature	water	°C	NA	0.2	±10%
Depth	water	Meters	NA	0.3	±15%
pH	water	SU	NA	0.2	±5%
DO	water	mg/L	NA	0.2	±5%
Specific conductance	water	µS/cm	NA	1% of range	±10%
Turbidity	water	NTU	NA	5% of range	±10%
Alkalinity	water	mg/L	1.0	10%	±20%
Ammonia Nitrogen	water	mg/L	0.004	10%	±20%
BOD	water	mg/L	2	10%	±20%
Chloride	water	mg/L	1	10%	±20%
Chlorophyll a	water	µg/L	0.1	20%	±30%
COD	water	mg/L	1	10%	±20%
E. Coli	water	org/100 ml	2	N/A	N/A
Enterococcus	water	org/100 ml	2	N/A	N/A
Hardness	water	mg/L	0.2	10%	±20%
Nitrate-Nitrite-N	water	mg/L	0.004	10%	±20%
Orthophosphate-P	water	mg/L	0.002	10%	±20%
Sulfate	water	mg/L	1	10%	±20%
Tannin/Lignin	water	mg/L	0.04	10%	±20%
Total Kjeldahl Nitrogen	water	mg/L	0.02	10%	±20%
Total Organic Carbon	water	mg/L	0.4	10%	±20%
Total Phosphorus	water	mg/L	0.002	10%	±20%
TSS	water	mg/L	0.5	10%	±30%

\* MDL values are in reference to methods with the lowest acceptable MDL found in the 2010 DCLS laboratory catalog. Certain parameters may have higher MDL values if using a different test method.

**Table 3. Data Quality Objectives for Metal Analyses**

Analyte	Matrix	Units	MDL*	Accuracy Goal	Precision Goal
Aluminum,dis.	water	µg/L	0.27	±30%	±20%
Antimony, dis.	water	µg/L	0.0014	±30%	±20%
Arsenic, dis.	water	µg/L	0.029	±30%	±20%
Cadmium, dis.	water	µg/L	0.014	±30%	±20%
Chromium, dis.	water	µg/L	0.048	±30%	±20%
Copper, dis.	water	µg/L	0.006	±30%	±20%
Iron(ICP), dis.	water	µg/L	0.6	±30%	±20%
Lead, dis.	water	µg/L	0.006	±30%	±20%
Magnesium(ICP), dis.	water	mg/L	0.007	±30%	±20%
Manganese, dis.	water	µg/L	0.006	±30%	±20%
Mercury, dis.	water	ng/L	0.35	±30%	±20%
Nickel, dis.	water	µg/L	0.007	±30%	±20%
Selenium, dis.	water	µg/L	0.06	±30%	±20%
Silver, dis.	water	µg/L	0.004	±30%	±20%
Thallium, dis.	water	µg/L	0.007	±30%	±20%
Zinc, dis.	water	µg/L	0.09	±30%	±20%
Aluminum	sediment	mg/kg	13	±30%	±20%
Antimony	sediment	mg/kg	0.02	±30%	±20%
Arsenic	sediment	mg/kg	0.4	±30%	±20%
Cadmium	sediment	mg/kg	0.02	±30%	±20%
Chromium	sediment	mg/kg	0.16	±30%	±20%
Copper	sediment	mg/kg	0.27	±30%	±20%
Iron	sediment	mg/kg	36	±30%	±20%
Lead	sediment	mg/kg	0.12	±30%	±20%
Manganese	sediment	mg/kg	1.4	±30%	±20%
Mercury	sediment	mg/kg	0.001	±30%	±20%
Nickel	sediment	mg/kg	0.17	±30%	±20%
Selenium	sediment	mg/kg	0.16	±30%	±20%
Silver	sediment	mg/kg	0.21	±30%	±20%
Thallium	sediment	mg/kg	0.01	±30%	±20%
Zinc	sediment	mg/kg	2.8	±30%	±20%

\* MDL values are in reference to methods with the lowest acceptable MDL found in the 2010 DCLS laboratory catalog. Certain parameters may have higher MDL values if using a different test method.

**Table 4. Data Quality Objectives for Organic Analyses**

Analyte	Matrix	Units	MDL*	Accuracy Goal	Precision Goal
Particle size	Sediment	%	N/A	N/A	20%
Total organic carbon	Sediment	g/kg	2.6	N/A	20%
PAHs	Sediment	µg/kg	Appendix A	40-140%	30%
PCB congeners	Sediment	ng/kg	Appendix A	40-140%	30%
Organochlorine pesticides	Sediment	µg/kg	Appendix A	40-140%	30%
Organophosphorus pesticides	Sediment	µg/kg	Appendix A	40-140%	30%
Herbicides	Sediment	µg/kg	Appendix A	40-140%	30%

\* MDL values are in reference to methods with the lowest acceptable MDL found in the 2010 DCLS laboratory catalog. Certain parameters may have higher MDL values if using a different test method.

## **A.8 SPECIAL TRAINING REQUIREMENTS/CERTIFICATIONS**

### ***A.8.1 Field Personnel Training***

Proper training of field personnel represents a critical aspect of quality control. Field technicians are trained to conduct a wide variety of activities using standardized protocols to ensure comparability in data collection among field teams and across geographic regions.

Entry level training is provided for new employees to ensure quality-related qualifications in field methods (such as instrument operation, approved sample collection, preservation, handling, field testing, and quality assurance procedures) and in computer skills such as station establishment, sample scheduling and data entry and retrieval. Training in field methods is provided by the WMA Quality Assurance Coordinator and experienced regional personnel. A team of Central Office personnel consisting of the DEQ data manager and other qualified personnel provides computer training.

All staff collecting water quality samples is required to complete formal training and/or testing modules on the procedures outlined in the most recent edition of the WMA SOP. Newly hired staff must complete training and pass testing within 12 months after hiring or before collecting chain of custody samples, whichever comes first. Staff who are certified must pass a test documenting their competency every two years.

Staff who fails to pass the certification test must discontinue sampling and be retrained and retested before being allowed to collect samples. New hires that do not successfully complete training will be paired with a mentor until they are able to successfully complete the test.

Training materials will include the use of PowerPoint presentations and hands on training. Course content will include all portions of the most recent edition of the WMA SOP as well as the use of the water monitoring module of the agency database (CEDDS) and chain of custody procedures.

When a boat is required for sample collection activities, the vessel operator must be an experienced boat handler and have completed the appropriate boating safety courses for the size class of vessels being utilized, as well as be well-versed in navigational skills and proficient in the use of GPS equipment. The vessel itself shall contain all the required U.S. Coastal Guard approved safety gear, possess current state registration, and be in good operational condition. Field staff assigned to work on a boat must pass a course in basic boat operations recognized by the United States Coast Guard or Virginia Game and Inland Fisheries.

Each field team member receives training to enable compliance with all applicable Occupational Safety and Health Administration or equivalent state or local regulation requirements.

### **A.8.2 Continued Proficiency**

To ensure continued proficiency in Quality Assurance/Quality Control procedures, the agency Quality Assurance Coordinator, or designee, performs a field audit of staff collecting samples. All field collection staff receives an audit at least once per two years. Staff performing monitoring for more than one type of program using significantly different protocols (example: riverine ambient and lake monitoring) may be audited more frequently.

### **A.8.3 Laboratory Personnel Training**

A written position description for each job in the laboratory is kept on record within the laboratory division. The position descriptions include the knowledge, skills, abilities and duties required of the position. A performance plan is prepared annually for each employee and their performance is evaluated by one interim and one final evaluation. Training is conducted at the division and group level. Performance evaluation samples are routinely used to determine proficiency in an area. It is the responsibility of the group manager to ensure orientation and rotation of workstation schedules. The division maintains a training record documenting each employee's credentials regarding education, seminars, workshops and on-site training. In order to assure competency and the ability to work independently, each employee is required to demonstrate completion of the following requirements:

1. Instruction in or prior knowledge of sample preparation, analysis and instrumentation principal associated with the method.
2. Instruction on the principles of laboratory safety associated with the method including review of associated MSDS forms.
3. Has read and understands the methods and SOPs associated with the analyses.
4. Instruction in or has prior knowledge of the instrument for the method.
5. Demonstrated performance of the method under the direct supervision of the trainer.
6. Instruction in or has prior knowledge of instrument and computer maintenance.
7. Independent successful completion of demonstration of capability.
8. Independent analysis of three sets of samples.

## **A.9 DOCUMENTATION AND RECORDS**

This QAPP will be distributed to each Regional Office and contract lab responsible for the collection of samples and generation of analytical data. The WMA QA Coordinator will be responsible for ensuring that any necessary changes required to keep the QAPP up to date with actual practices are documented and implemented. The QA Coordinator is also responsible for ensuring that a distribution list of QAPP recipients is maintained, such that revisions and updates can be distributed. The document control format used in this QAPP will identify the QAPP revision number and revision data. A QAPP revision history will be maintained that identifies each revision and changes to the program throughout its implementation.

### ***A.9.1 Field Data Documentation***

The VADEQ water monitoring and assessment program requires that each data generating activity be thoroughly documented. Field staff record field data in hardcopy form using field data sheets containing station ID, date and time collected, survey depth, collector, group code, and the field measurement results. At the end of each sampling day, all the field data are transcribed into the DEQ Comprehensive Environmental Data System (CEDS) database. Field data sheets will be secured in filing cabinets at Regional Offices and maintained for a seven year period.

### ***A.9.2 Equipment Calibration and Maintenance***

Procedures for operating, maintaining and calibrating instruments used in field environmental measurements are contained in the WMA SOP manual. Personnel using field instruments are expected to read and be thoroughly familiar with all procedures detailed in the standard operating procedures. In particular, the program manager shall meticulously follow the calibration procedures given in the standard operating procedures. A calibration and maintenance logs shall be kept for each instrument. Dates of calibration and any other pertinent data shall be routinely entered in the logbook. All maintenance activities will also be entered in the logbook. Calibration log and maintenance records shall be maintained for seven years at either the Regional Office or Central Office.

### ***A.9.3 Laboratory Data Documentation***

Documentation for analytical data is kept on file at the participating laboratories and recommended to be maintained for five years. These files should be stored such that they are always available and reviewed during external audits. These records include the analyst's comments on the condition of the sample and progress of the analysis, primary standard certification, working standard preparations, instrument calibration results, results of QC check sample/ measurements, chromatograms or instrument printouts, and final data calculations.

Laboratory analytical data that are received from DCLS or other contract laboratories have undergone extensive laboratory QA/QC procedures. The Virginia Information and Technology Agency (VITA), or designated personnel, will ensure automated upload of analytical data from the DCLS LIMS database into the VADEQ central database (CEDS) daily. Contract laboratories not utilizing a LIMS database system provide analytical results to VADEQ via printouts or electronic files utilizing a commonly accepted ASCII file format such as a comma delimited text file or a Microsoft Excel spreadsheet. This data is either entered into CEDS manually or by batch upload.

## **B.1 SAMPLING PROCESS DESIGN**

### **B.1.1 Site Locations:**

#### **B.1.1.1 Watershed Stations**

Watershed stations are established to provide statewide, comprehensive monitoring coverage of the commonwealth's streams by hydrologic units. Watershed stations consist of two types, watershed mouth stations and intra-watershed stations. Stations are geographically targeted to minimize bias in site selection, and effectively provide a census of state's local watersheds. They provide data to assess the quality of water within the watershed, the upstream water entering the watershed, the downstream water as it exits the watershed. Intra-watershed stations are rotated within the watershed to eventually provide monitoring data in all major tributaries in the watershed. The number of stations monitored in a watershed is based on the watershed's size and its NPS priority ranking. Typically, one station is located per 10,000 acres of a high priority area. One station is located per 20,000 acres of a medium priority watershed. Finally, one station is located per 30,000 acres of low priority watersheds.

The priority ranking of the watersheds is completed biennially by Department of Conservation and Recreation. The densities of stations suggested here would produce approximately 1200 stations statewide per six year rotation, with a distribution such that approximately 50% of the stations would be located in high priority watersheds, which represent approximately 30% of the land area of the state.

#### **B.1.1.2 Trend Stations**

Trend stations provide the data for detecting and evaluating tendencies in long-term water quality changes. Listed below are desirable characteristics for trend station site selections:

##### **A. Free-flowing, freshwater stream:**

1. Whenever possible, stations should be located in direct association with a flow gauge. Otherwise, stations should be near enough to one or more gauges to permit adequate interpolation of discharge at the site. When gauging is not available, a gauging device should be installed or an alternative means of flow measurement should be utilized.
2. For water quality trend assessment, sites should be located near the mouths of the watershed to evaluate the loadings being discharged to subsequent (downstream) watersheds. The location of such stations may be either upstream from the outflow of one watershed, or downstream from the inflow to the subsequent watershed, but an effort should be made to minimize the number of significant tributaries that enter the gauged stream between the monitored site and the watershed boundary. On a mainstream river consisting of waters from multiple upstream watersheds, the site location should be:

- i. At or near the boundaries of USGS Cataloging Units (8-digit HUCs)
- ii. At or near the stream or river's fall line, when one exists, and
- iii. Immediately above the freshwater head-of-tide, when it exists, with the same restrictions as those described in item 1 above.

#### B. Tidal waters

For evaluating trends in tidal fresh and saltwater tributaries, a trend station should be located near the geographic center of the tributary, and far enough from the mouth so that a minimum of open estuary or oceanic water is sampled at flood tide. Such samples should be representative of the tributary and not the estuary or ocean. In open estuarine areas, trend stations may be located at or immediately upstream from the stream's convergence with the open estuary or ocean, or in the mainstream of a bay/embayment, in order to evaluate estuarine water quality trends.

#### C. All waters

Trend stations should be located outside the mixing zone of permitted discharges and sufficiently downstream from significant tributaries to permit the complete mixing of the combined water columns. Whenever possible, sites should be located where adequate biological monitoring can be accomplished.

### ***B.1.2 Sample Number and Types***

The water quality monitoring network consists of approximately 910 stations annually ( about 400 watershed stations, 400 trend stations, 110 probabilistic stations) for which approximately 20,000 water column samples are collected each year. In addition to field measurements performed by VA DEQ monitoring staff, the DCLS performs approximately 30,000 analyses on submitted samples annually. All stations are sampled for the parameters as listed in Table 1.

Most of the stations are located at bridge crossings and can be identified using route numbers or by noting latitude and longitude. Estuaries and other large water bodies are monitored by boat and sites are located using latitude and longitude. The water column sampling points are generally mid-channel, or as determined by field staff to be representative of the water body. Sampling locations are sites:

1. Where flow is significant enough to ensure a relatively well-mixed, homogenous sample
2. Outside of effluent mixing zone
3. On the upstream side of the bridge whenever possible
4. Not directly below large amounts of debris or other temporary obstructions.

Field staff determine station locations prior to sampling and perform reconnaissance on the sites to determine accessibility. If a trend station location is inaccessible during a sampling event, field staff should not sample a nearby location such as the next bridge crossing but should return at another time to sample the site. Long term inaccessibility to a sample site, such as due to bridge

construction, should be assessed by the regional water quality monitoring manager for consideration of a temporary suspension or permanent discontinuation of the station. It is important that trend stations are not moved without sufficient reason to provide an uninterrupted long term record. If for some reason the trend station needs to be moved, a comparison study needs to be conducted to ensure comparability of the data.

### ***B.1.3 Sampling Frequency***

Watershed stations are sampled for core indicators bimonthly over a two-year period. Resources permitting, sediment samples may be obtained once during the two-year period for metals and toxic organic compound contamination testing (e.g. pesticides, PCB etc.). Trend stations are sampled for core indicators bimonthly. When resources permit, sediment samples may also be obtained once every five or six years for metals and toxic organic contamination testing. Probabilistic samples are collected once per year for water column and when resources allow, sediment samples for select parameters.

### ***B.1.4 Source of Variability***

Potential sources of variability include field methodology, laboratory analyses and seasonal variability. To reconcile these potential sources of variation, Central Office provides a SOP Manual to all regional personnel and requires field duplicates to be collected by each Regional Office. This provides a uniform method of sampling and tests for individual variation to ensure comparability within and across regional boundaries. Laboratory personnel are also required to analyze samples in replicate to ensure sound laboratory procedures are utilized. Finally, to address seasonal variation, samples are collected year round to ensure each season is adequately represented.

## **B2. Sampling Methods Requirements**

The WMA SOP manual (revision 18; Appendix B of this QAPP) provides the following information:

- Process for cleaning and decontamination of sampling equipment
- Preventive maintenance
- Preparation of sample containers
- Quality assurance procedures
- Field sample collection procedures and methods
- Field analyses
- Sample handling
- Safety for equipment and personnel

The types of samples/matrices, sample containers, sample volumes, field preservation, analysis methods and maximum holding times are summarized in Table 5.

### B.2.1 Corrective Action for Field Activities

Field sampling staff has the primary responsibility to document failures in the sampling or measurement systems. Deviations from WMA SOP are documented in the comment section in the field data sheet. If monitoring equipment fails, WMA field staff will report the problem in the comment section of the field data sheet and will not record data values for the variables in question. Actions will be taken to replace or repair broken equipment prior to the next field use. No data will be entered into the database that are known to have been collected with a faulty instrument.

**Table 5. Sample Matrix, Containers, Required Volumes, Field Preservation and Holding Time Summary**

Parameter for Analysis	Matrix	Recommended Containers	Typical Sample (ml)	Field Preservation	Maximum Holding Time
Alkalinity	Water	Polyethylene bottle	250 ml	4°C	14 days
Ammonia-N	Water	Polyethylene bottle	250 ml	4°C	24 hrs
BOD	Water	Polyethylene bottle	2000 ml	4°C	24 hrs
Chloride	Water	Polyethylene bottle	250 ml	4°C	28 days
Chlorophyll a	Water	Aluminum foil	N/A	Filter, 4°C, keep dark	30 days (-20°C)
COD	Water	Polyethylene bottle	250 ml	1 ml conc. H <sub>2</sub> SO <sub>4</sub> to pH<2, 4°C	28 days
Dis. Mercury	Water	Perfluorinated plastic bottle	125 ml	4°C, no air gap	28 days
Dis. Metals (except Mercury)	Water	Plastic wide mouth bottle with special top	1000 ml	4°C, no air gap	180 days
E. Coli	Water	Sterile bottle	125 ml	4°C	24 hrs
Enterococci	Water	Sterile bottle	125 ml	4°C	30 hrs
Hardness	Water	Polyethylene bottle	250 ml	1 ml conc. HNO <sub>3</sub> to pH<2, 4°C	6 months
Nitrate + Nitrite-N	Water	Polyethylene bottle	250 ml	4°C	24 hrs
Orthophosphate-P	Water	Polyethylene bottle	250 ml	4°C	48 hrs
Sulfate	Water	Polyethylene bottle	250 ml	4°C	28 days
TKN	Water	Polyethylene bottle	250 ml	1 ml conc. H <sub>2</sub> SO <sub>4</sub> to pH<2, 4°C	28 days
TOC	Water	Glass vial	40 ml	1 ml conc. HCL to pH<2, 4°C	28 days
Total Mercury	Water	Plastic wide mouth bottle	125 ml	4°C, no air gap	28 days
Total Metals	Water	Plastic wide mouth bottle with special top	1000 ml	4°C, no air gap	180 days
Total Phosphorus	Water	Polyethylene bottle	250 ml	1 ml conc. H <sub>2</sub> SO <sub>4</sub> to pH<2, 4°C	28 days
TSS	Water	Polyethylene bottle	1000 ml	4°C	7 days
Particle Size	Sediment	Plastic wide mouth jar	125 ml	4°C, up to 6 months	28 days
Synthetic Organic Compounds	Sediment	Pre-cleaned amber glass jar with Teflon lid-liner	250 ml (2 jars)	4°C, up to 14 days	12 months <sup>1</sup> (-20°C)
TOC	Sediment	Pre-cleaned clear glass jar	125 ml	4°C, up to 28 days	12 months <sup>1</sup> (-20°C)
Trace metals	Sediment	Pre-cleaned clear glass jar with Teflon lid-liner	250 ml	4°C, up to 180 days	12 months <sup>1</sup> (-20°C)

(1) Sediment samples for metal, organic and TOC analysis may be refrigerated at 4°C for up to 14 days maximum. Analysis must start within the 14 day period or the sample must be stored frozen at -20°C for up to 12 months.

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

Proper sample handling procedures for water and sediment samples are provided in the WMA SOP. WMA CEDS database contains additional information regarding the sample containers used, required volumes, field preservations and maximum holding times for each analyte sampled for by VADEQ. Table 5 provides a summary of this information for water and sediment samples.

### ***B3.1 Sample Identification***

Sample identification consists of station name, collection date and time, collector and sample depth sample. The station name is composed of a numerical code identifying the major river basin on which the tributary is located followed by a dash (e.g. 8- for the York River Basin), a three letter code for the stream from which the sample is obtained (e.g. PMK for the Pamunkey River) and a five digit numerical value identifying the station location in river miles to the nearest 100<sup>th</sup> of a mile from the mouth of the stream (e.g. 013.10). Large stream systems may be further subdivided into major segment or sub-basin by substituting the dash with a letter. Field staff schedule the sampling run ahead of the time and utilize the CEDS database to print the sample bottle labels and field sheets before the sampling event. The label contain the following information: station ID, date and time collected, survey depth, collector, group code and preservation. After a given sample has been collected and, if needed, the preservation has been added, a self-adhesive, waterproof label will be affixed to the container. If the label cannot be affixed to the container the labels should be placed on a sample tag and then attached to the container.

### ***B3.2 Sample Packing***

Unless specified otherwise, in the field, all samples will be packed in wet ice during shipment; to ensure they are kept at approximately 4<sup>0</sup>C. Sample containers will be labeled clearly with printed labels or sample tags. All sample container caps and lids will be checked for tightness prior to placement in the cooler.

Prior to shipping, the field staff drain excess water from the cooler and refill the ice to maintain the samples at 4<sup>0</sup>C during transport. Samples are shipped in the cooler via a contracted courier or shipping service to DCLS or another contracted laboratory. For most samples, coolers are delivered to the laboratory by next day. Upon receipt of the samples, the laboratory transfers them to the refrigerator set at 4<sup>0</sup>C for storage until analyzed. Handling, preparation, transport, and storage of samples are done in a manner to minimize bulk loss, analyte loss, contamination or biological degradation.

### ***B3.2 Sample Chain of Custody***

Sample custody procedures are an integral part of laboratory and field operations. Since routine ambient monitoring data are not used for legal purposes, formal chain of custody procedures are not required. Samples designated for chain of custody handling are transported in secured,

locked COC coolers or regular sample coolers sealed with tape prior to shipping. It is assumed that samples in tape-sealed ice cooler are secure whether being transported to DCLS by field personnel, common courier, or by commercial package delivery.

For samples which may be used for legal purposes, formal chain of custody procedures are followed. Section 4.12 of the WMA SOP manual contains instructions for field teams when handling and shipping chain of custody samples.

DCLS is responsible for sample custody upon receipt of samples at DCLS central receiving by Sample Records Management (SRM) staff. Laboratory procedures for sample processing are described in detail in the individual DCLS section's SOPs. Once samples are received by the laboratory, the SRM staff members check the sample bottle labels against the corresponding information in the LIMS. The SRM notes any damaged or missing sample containers and checks for chemical preservation of samples requiring the addition of acid by recording the pH of the sample during the sample login process. A temperature bottle blank, included in each cooler of samples, is measured and recorded at the time of sample receipt by the lab personnel to ensure the samples are preserved at 4 °C. Any discrepancies in sample identifications, sample analysis information, missing samples, or any indication that samples are not properly preserved to the correct pH or temperature is communicated to the VADEQ WMA Laboratory Liaison.

## **B4 ANALYTICAL METHODS REQUIREMENTS**

The analytical methods used by DCLS and contract laboratories for this program are in accordance with currently approved procedures given in Standard Methods for Examination of Water and Wastewater, Methods for Chemical Analysis of Water and Wastes or with other procedures approved or accepted by the USEPA. Analytical methods and approximate data turnaround times are described in Table 6. A description of the analytical equipment and instrumentation required for each analysis is included in the individual laboratory technical procedure manuals for the methods.

When problems occur during the analytical process, a corrective action is implemented. The corrective action should identify the source of the problem and eliminate it. It is encouraged for action to occur at the lowest level to resolve problem. Staff communicates corrective actions to management and documented for quality assessment to determine if additional corrective actions are necessary. A copy of a corrective action form used by VADEQ is provided in Appendix C.

The laboratory supervisor of each lab has the primary responsibility for responding to failure of analytical systems to the DEQ Laboratory Liaison. Solutions which are consistent with the measurement objectives will be reached in consultation with WMA QA Coordinator.

Failures in field and laboratory measurement systems involve, but are not limited to, such things as instrument malfunctions, failures in calibration, sample jar breakage, blank contamination, and quality control samples outside of defined limits (listed in Tables 7-11). In many cases, field staff or lab analysts are able to correct the problem. If the problem is resolvable by field staff or lab analysts, then they document the problem in their field data sheet or laboratory record and

complete the analysis. If the problem is not resolvable, then it must be conveyed to the respective supervisor, who makes the determination if the problem compromised the sample analysis and should therefore results not be reported. The nature and disposition of the unresolved problem needs to be documented in the data report that is sent to the WMA QA Coordinator.

Unused raw sample volume, sample extract and sample digestates is disposed of properly in accordance with each laboratory's waste management procedures. Disposal of unused raw sample for routine analysis will occur when the analysis is complete and verified to be accurate or when holding times are exceeded, whichever is less. Formal Chain of Custody samples are maintained until disposal is approved by DEQ or until holding times are exceeded, whichever is less.

**Table 6. Analytical Methods and Approximate Data Turnaround Time for WMA Program**

Parameters	Matrix	Analytical Method	Approx. Data Turnaround Time
Alkalinity	Water	SM 2320B/4500H+B	21 days
Ammonia-N	Water	EPA 350.1, USGS I-2523-85	14 days
BOD	Water	SM 5210 B	21 days
Chloride	Water	EPA 300.0	21 days
Chlorophyll a	Water	EPA 446.0	21 days
COD	Water	ASTM D1252-95B	21 days
Dis. Mercury	Water	EPA 245.7	28 days
Dis. Metals (except Mercury)	Water	EPA 1638	28 days
E. Coli	Water	EPA 1103.1	7 days
Enterococcus	Water	EPA 1600	7 days
Hardness	Water	EPA 200.7, 1638	21 days
Nitrate+Nitrite-N	Water	EPA 353.2, USGS I-4545-85	14 days
Orthophosphate -P	water	EPA 300, 365.1	14 days
Sulfate	Water	EPA 300.0	21 days
TKN	Water	EPA 351.2	14 days
TOC	Water	SM 5310 B	21 days
Total Metals	Water	EPA 1638	28 days
Total Phosphorus	Water	EPA 365.4	21 days
TSS	Water	USGS I-3765-85	21 days
Herbicides	Sediment	EPA 8151	54 days
Mercury	Sediment	EPA 3051B (digestion), EPA 245.1	28 days
Organochlorine pesticides	Sediment	EPA 8270	54 days
Organophosphorus pesticides	Sediment	EPA 8270	54 days
PAHs	Sediment	EPA 8270	54 days
Particle size	Sediment	Applied Marine Research Lab	21 days
PCB congeners	Sediment	EPA 8270	54 days
TOC	Sediment	SM 5310B	21 days
Total Metals (except Mercury)	Sediment	EPA 200.7	28 days

## B5 Quality Control Requirements

Data Quality Objectives (DQOs) are quantitative and qualitative statements specifying the quality of the environmental data required to support the decision making process. The intended use of the data, analytical measurements and the availability of resources are an integral part in the development of the DQOs. DQOs define the total uncertainty in the data that is acceptable for each specific activity during sample events. The uncertainty includes both sampling error and analytical instrument error. Ideally, the prospect of zero uncertainty is the objective; however, the variables associated with the collection process (field and laboratory) inherently contribute to the uncertainty of the data. The overall quality assurance objective is to keep the total uncertainty within an acceptable range that will not hinder the intended use of the data. In order to achieve this objective, it is necessary to specify data quality requirements such as detection limits, criteria for accuracy and bias, sample representativeness, data comparability and data completeness. The overall objectives and requirements for this program have been established to assure a high degree of confidence in the data obtained. Tables 7-11 contain the data acceptability criteria used in this program.

### **B.5.1 Field QC Samples**

QA/QC samples will be collected in the field to allow evaluation of data quality. Field QA/QC samples include equipment blanks, field split samples and preservative reagent blanks.

#### **B.5.1.1 Equipment Blanks**

To ensure the effective cleaning of sampling devices, fill the device with clean sand or deionized water or pump deionized water through the device and transfer the sand or deionized water to the appropriate sample container. Preserve the sample as would be done for a regular sample and return it to the laboratory for analysis. The equipment blank should be processed at the beginning of the sampling day. This may be performed in the Regional Office prior to going to field. If the sample is collected straight from the source and not by a sampling device, then the equipment blank is not necessary. Equipment blanks will be collected for all required parameters at a rate of 4% of the number of total stations within annual run schedule or more frequently if specified for a special study. If the analytes of interest are detected at levels greater than three times of MDL, the field staff should be notified so that the source of contamination can be identified (if possible) and corrective measures taken prior to the next sampling event. If the concentration in associated samples is less than five times the value in the equipment blank, the results for the environmental samples may be affected by contamination and should be qualified.

#### **B.5.1.2 Field Split Samples**

Split samples should be collected for all the parameters at a rate of 4% of the total number of stations within annual run schedule or more frequently if specified for a special study. The split sample will be collected in the same manner as the regular sample and from the same sampling device. Field split samples are collected to determine the homogeneity of the sampling device and consistency of sample handling, within the limits and constraints of the situation. For non bacteria samples, field split results will be assessed using the relative

percent difference (RPD) between replicate measurements. RPD limits for laboratories are stated in the Table 2-4. The RPD will be calculated as follows:

$$\text{RPD} = (200) (X_1 - X_2) / (X_1 + X_2)$$

Where  $X_1$  is the larger of the two observed values and  $X_2$  is the smaller of the two observed values.

For bacteria samples, RPD is not as useful of a quality assurance check due to the natural variability of bacteria in the environment and the tendency for bacteria to cling to solids. As a screening check of field sampling performance, the highest of the two or more split samples collected at the site during the sample event should be less than or equal to 10 times the value of the lowest split sample value. For samples that are greater or less than the reported detection limit, the absolute reported value is used.

### B.5.1.3 Preservative Reagent Blanks

In order to ensure a preservative is contaminant free, it must be tested before it is used for sample preservation. Submit a preservative reagent blank to DCLS prior to using a new lot of preservative in the field.

## **B.5.2 Laboratory QC Sample**

### B.5.2.1 Laboratory Method Blank

The purpose of analyzing method blanks is to ensure sample contamination has not resulted from laboratory solvents, reagents or glassware used in processing the samples during the analytical process. Method blanks are prepared and analyzed by the laboratory at a rate of at least one per analytical batch. The method blank is processed through the entire analytical procedure in a manner identical to the samples. Method blank criteria are provided in Tables 7-11. If the blank indicates contamination has occurred and eliminating the contamination is not possible, all impacted analytes in the analytical batch shall be flagged or the associated samples should be reanalyzed. In addition, a detailed description of the contamination source and the steps taken to eliminate/minimize the contaminants shall be documented. Subtracting method blank results from sample results is not acceptable.

### B.5.2.2 Matrix Spike and Matrix Spike Duplicate

A laboratory matrix spike (MS) and a matrix spike duplicate (MSD) is used to evaluate the effect of the sample matrix on the recovery of the compound(s) of interest and to provide an estimate of analytical precision. Specifications for MS and MSD'S for water chemistry and sediment samples are provided in Tables 7-10. For bacteria samples, a MS and MSD check is not applicable.

A field sample is first homogenized and then split into three subsamples. Two of the subsamples are fortified with the matrix spike solution and the third subsample is analyzed to

provide a background concentration for each analyte of interest. The final spiked concentration of each analyte tested in the sample is at least five times the MDL for that analyte. Additionally, the total number of spikes performed should cover the range of expected concentrations. Recovery is the accuracy of an analytical test against a known analyte addition to a sample. Recovery is calculated as follows:

$$\%R = (100) (X_S - X) / T$$

Where  $X_S$  is the measured value of the spiked sample,  $X$  is the measured value of the unspiked sample, and  $T$  is the true value of the spike solution added.

Recovery data for the fortified compounds ultimately provides a basis for determining the prevalence of matrix effects in the samples. If the percent recovery for any analyte in the MS or MSD is less than the recommended limit, the chromatograms (in the case of trace organic analyses) and raw data will be reviewed. If an explanation for a low percent recovery value is not discovered, the instrument response may be checked using a calibration standard. Low matrix spike recoveries may be a result of matrix interference and further instrument response checks may not be warranted, especially if the low recovery occurs in both the MS and MSD, and the other QC sample in the batch indicate that the analysis was “in control”. An explanation for low percent recovery values for MS/MSD results, corrective actions taken and verification of acceptable instrument response will be included in the data package. Analysis of MS/MSD is also useful for assessing laboratory precision. The RPD between MS and MSD results should be less than the precision goal listed in Tables 2-4 for each analyte of interest.

### B.5.2.3 Laboratory Control Spikes

Laboratory Control Samples (LCSs) consist of laboratory fortified method blanks. The purpose of analyzing Laboratory Control Samples (LCSs) is to demonstrate the accuracy of the analytical method. LCSs are analyzed at rate of one per sample batch. The accuracy criteria are listed in Tables 7-11. For bacteria samples, laboratory positive and negative controls are used in place of LCS. If the recovery is outside the specified range, the analytical process is not being performed adequately for that analyte and the sample batch must be re-processed and the LCS reanalyzed. If a reanalysis is not possible, the associated sample results should be qualified as biased low or high.

**Table 7. Acceptability Criteria for Conventional Constituents in Water**

Sample type	Frequency of Analysis	Acceptance Criteria	Recommended Corrective Action
External Calibration (3-5 standards over the expected range of sample)	Follow manufacturer's or lab procedures in specific analytical protocols.	Correlation Coefficient $\geq 0.995$	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Calibration Check Standard (Minimum of one mid-range standard prepared independently from initial calibration standard)	After initial calibration or recalibration. Every 20 samples	90-100% Recovery	
Reference Materials	One per analytical batch	Measured value <95% confidence intervals if certified. Otherwise, 80-120% Recovery	
Laboratory Blanks (method, processing, bottle, reagent)	One method blank per analytical batch	Not to exceed 3x MDL	Determine cause of problem, remove sources of contamination, and reanalyze all suspect samples or flag all suspect data
Matrix Spike	One per 20 samples or one per batch, whichever is more frequent	80-120% Recovery or within 3x standard deviation of laboratory's actual method recoveries.	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data. 0% recovery requires rejection of all suspect data.
Matrix Spike Duplicate	One per 20 samples or one per batch, whichever is more frequent	RPD < 20%	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Laboratory Control Sample	One per analytical batch	80-120% Recovery	
Laboratory Duplicate	One per 20 samples or one per batch, whichever is more frequent	RPD < 20%	
Field Equipment Blanks (EB)	4% of the total stations per analytical procedure per year.	Not to exceed 3x MDL	Determine cause of problem (e.g. improper cleaning, exposure to airborne contaminants), remove sources of contamination, and reanalyze all suspect samples or flag all suspect data
Field Split Samples	4% of total samples per analytical procedure per year	RPD < 30%	Determine cause and take appropriate corrective action. Reanalyze all suspect samples or flag all suspect data

**Table 8. Acceptability Criteria for Trace Metals in Water including Mercury**

Sample type	Frequency of Analysis	Acceptance Criteria	Recommended Corrective Action
External Calibration. Minimum three point calibration. Each set up, major disruption, and when routine calibration checks exceed specific control limits	Follow manufacturer's or lab procedures in specific analytical protocols.	Correlation Coefficient $\geq 0.995$	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Calibration Check Standard (minimum of one mid-range standard prepared independently from initial calibration standard)	After initial calibration or recalibration. Every 10 samples	90-110% Recovery	
Reference Materials	One per analytical batch	Method validation and routine accuracy assessment 75 – 125% Recovery	If matrix spikes are in control then proceed. If not, determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Matrix Spikes (Predigestion spike, postdigestion spike)	One per 10 samples	Predigestion= 70–130% Recovery  Postdigestion= 80-120% Recovery	If reference materials are in control then proceed. If not, determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Matrix Spikes Duplicate	One per 10 samples	RPD < 20%	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Laboratory Duplicates	One per 20 samples or one per batch, whichever is more frequent	RPD < 20%	
Laboratory Control Sample	One per analytical batch	85-115% Recovery	
Laboratory Blanks (method, processing, bottle, reagent)	One method blank per analytical batch	Not to exceed reporting limit	Blanks found above the MDL below the RL are investigated to prevent significant contamination from occurring
Equipment Blanks (EB)	Will be collected in the field at rate of 10% of the total stations	Not to exceed reporting limit	
Field Duplicates	10% of total samples per analytical procedure per year	RPD < 30%	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data

**Table 9. Acceptability Criteria for Sediment Trace Metals Including Mercury**

Sample type	Frequency of Analysis	Acceptance Criteria	Recommended Corrective Action
External Calibration. Minimum three point calibration. Each set up, major disruption, and when routine calibration checks exceed specific control limits	Follow manufacturer's or procedures in specific analytical protocols.	Correlation Coefficient $\geq 0.995$	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Calibration Check Standard (Minimum of one mid-range standard prepared independently from initial calibration standard)	After initial calibration or recalibration. Every 10 samples	90-110% Recovery.	
Reference Materials	One per analytical batch	Method validation and routine accuracy assessment 75 – 125% Recovery	If matrix spikes are in control then proceed. If not, determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Matrix Spikes (Predigestion spike, postdigestion spike)	One per 10 samples	Predigestion= 70 – 130% Recovery Postdigestion= 75-125% Recovery	If reference materials are in control then proceed. If not, determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data
Matrix Spikes Duplicate	One per 10 samples	RPD < 35% for Mercury, all other metals RPD<25%	Determine cause and take appropriate corrective action. Recalibrate and reanalyze or flag all suspect samples or data.
Laboratory Duplicates	One per 20 samples or one per batch, whichever is more frequent	RPD < 20%	
Laboratory Control Sample	One per analytical batch	85-115% Recovery	
Laboratory Blanks( method, processing, bottle, reagent)	One method blank per analytical batch	Not exceed reporting limit	Blanks found above the MDL below the RL are investigated to prevent significant contamination from occurring
Equipment Blanks (EB)	Will be collected in the field at rate of 10% of the total stations	Not exceed reporting limit	
Field Duplicates	10% of total samples per analytical procedure per year	RPD < 30%	Determine cause and take appropriate corrective action. Recalibrate and reanalyze or flag all suspect samples or data.

**Table 10. Acceptability Criteria for Sediment Organic Compounds (PCB, PAH, OC, OP)**

Sample type	Frequency of Analysis	Acceptance Criteria	Recommended Corrective Action
Initial Calibration	Initial to calibrate the instrument and then whenever the CCC fails	RRF must be $\geq 0.05$ and the percent relative standard deviation (%RSD) must be $\leq 30\%$ . Four compounds from calibration group may be $< 40\%$ if min RRF.0.01. Analyst may use linear and sometimes quadratic curves (min. of 6 points) as long as the Corr. $> 0.99$ (linear) and R.0.995 (quad)	Stop analysis, take corrective action (prepare new standards, perform instrument maintenance), recalibrate by re-injecting the calibration standards.
Calibration Check Standard (Min. of one mid-range standard prepared independently from initial calibration standard)	Analyzed at the beginning of an analytical sequence and is good for 12 hrs shift	For 90% of the compounds per fraction, RRF must be $\geq 0.05$ and the percent difference between the calculated amount and the true value for each analyte must not exceed $\pm 25\%$ . For the remaining 10% the analytes, the percent difference must not exceed $\pm 35\%$	Re-inject the calibration check standard once. If it still fails, recalibrate by re-injecting the calibration standards.
Performance Evaluation Samples	Minimum of one per year	Limits provide by vendor, typical 75-125%	Evaluate during data validation, No immediate corrective action possible.
Method Blank	One per preparation batch	Not to exceed RL	Reanalyze the method blank once. If analyte is still over RL, re-extract and reanalyze any samples that have values that are less than ten times the levels in the blank.
Internal standard	Each sample	Internal standard area counts must not deviate by more than a factor of two (9-50% to 100%) from either the mid-point standard of the initial calibration or the last CCC.	Re-inject the sample extract. If it still fails, qualify all compounds associated with the failing internal standard(s).
Surrogate Standards	Each sample	Recovery must be within the range of 30-150%. If there are two surrogates, at least one must be 30-150% and the other $> 10\%$ . If there are three surrogates, two must be 30-150% and the other $> 10\%$ .	If the recovery is 10-30%, qualify all compounds associated with that fraction. If the recovery is less than 10%, re-extract the sample for that fraction.
Matrix Spike	Once per batch or once per matrix type	Recovery should be in the range of 40-140% for at least 80% of the analytes.	Re-extract and reanalyze another MS/MSD. If homogeneity is an issue choose another sample.
Matrix Spike Duplicates	Once per batch or once per matrix type	Recovery should be in the range of 40-140% for at least 80% of the analytes. Compare to matrix spike results RPD should be $\leq 30\%$ for 80% of the analytes.	Re-extract and reanalyze another MS/MSD. If homogeneity is an issue choose another sample.

**Table 10 Continued**

<b>Sample type</b>	<b>Frequency of Analysis</b>	<b>Acceptance Criteria</b>	<b>Recommended Corrective Action</b>
Laboratory Control Sample – sand spike	Once per batch	70% of the target compounds should be within $\pm 35\%$ of the true value.	Evaluate the lab control sample in conjunction with the MS/MSD results. If the MS/MSD results are acceptable, re-extract another lab control sample. If the MS/MSD is unacceptable, re-extract all samples and QC associated with the batch.
Target Analyte List (TAL) Identification	All detected TAL's in samples	Mass ratio of primary ion to secondary ion must be within 20% of the expected value.	NA
Field Split Samples	One per ten samples	RPD should be $< 40\%$ .	Evaluate during the data validation. No immediate corrective action possible.

**Table 11. Data Acceptability Criteria for Bacteria-Pathogen in Water Sample**

<b>Sample type</b>	<b>Frequency of Analysis</b>	<b>Acceptance Criteria</b>	<b>Recommended Corrective Action</b>
Field Duplicates	4% of total bacteria samples per year	$\leq 10x$ difference between the highest split and lowest split from the same sample event.	Determine if problem was due to sampling process or from natural conditions. Take appropriate corrective action if needed. Flag all suspect data.
Lab Method Blanks (Sterility Checks)	One per batch	$<$ reporting limit	Identify contamination source. Check reagents. Re-analyze blank
Lab Duplicate	One per batch	$R_{\log} \leq 3.27 * \text{mean } R_{\log}$	Recalibrate and reanalyze
Lab Negative Control Samples	One per culture medium or reagent lot	$<$ reporting limit	Identify source. Clean equipment and prepare new media. Re-examine negative control.
Lab Positive Control Samples	One per culture medium or reagent lot	$\geq$ reporting limit	Identify and correct problem. Re-examine positive control.

## **B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements**

To minimize downtime of measurement systems, all field and laboratory instrument/equipment must be maintained in working condition. Environmental Field Specialists and laboratory technicians inspect instruments and equipment in the lab daily. Corrective action is immediately taken when problems are found. Backup instruments /equipment or common spare parts will be available so that if any piece of equipment fails during use, repairs or replacement can be made as quickly as possible and the measurement tasks resumed.

### ***B.6.1 Field Instrument /Equipment***

All field instrument/equipment having manufacturer recommended schedules of maintenance will receive preventive maintenance according to that schedule. Environmental Field Specialists in each Regional Office have the responsibility to ensure the preventive maintenance schedule listed in the WMA SOP is followed. Other equipment used only occasionally will be inspected at least monthly and especially prior to being taken into the field for availability of spare parts, cleanliness, battery strength, etc. Common spare parts which should be available in the lab include, but are not limited to batteries, tubes, rubber tubing, o-rings, membranes, electrolyte, and replacement probes. If performance checks or calibration procedures indicate that a problem exists, appropriate maintenance must be conducted immediately or the equipment is returned to the manufacturer for service. Defective equipment will not be used operationally until repaired and satisfactory performance results are achieved.

### ***B.6.2 Laboratory Instrument/Equipment***

The primary goal of the laboratory's preventative maintenance programs is to prevent instrument and equipment failure and to minimize instrument down time when failure occurs. The laboratories maintain an inventory of replacement parts needed for preventative maintenance and spare parts that routinely need replacement (e.g. septa, gauges, source, detectors etc.). Implementation and documentation of the preventative maintenance program according to the laboratory preventative maintenance policies in the QA Plan is primarily be the responsibility of analysts using the instrumentation.

A preventive maintenance logbook is maintained in the Regional Offices documenting maintenance performed on each instrument. The regional program coordinator periodically reviews the logbook to identify equipment with high repair records and to determine which specific items require the most frequent repairs or replacement. Depending on the difficulty of replacement, these items should be added to the list of critical spare parts to be maintained at the Regional Office.

SOPs for preventive maintenance of field equipment and the required documentation are contained in the WMA SOP.

## **B7 Instrument Calibration and Frequency**

Field and laboratory equipment and instruments require routine calibration checks to verify that their performance is within acceptable quality standards. The following sections will discuss procedure and frequency for instrument calibrations.

### ***B.7.1 Field Operations:***

The field multiprobe instrument must be calibrated prior to each sampling event. Regional offices maintain a calibration logbook for each multiprobe. Each book contains a set of instructions on how the calibration should be performed and a chart for documentation of calibration date, time, pH standards used, saturated dissolved oxygen, temperature, barometric pressure reading, conductivity calibration reading, initials of personnel, and comments. The chart documents morning calibration results and calibration checks performed at the end of each sampling day. A brief summary of the requirements for calibration by parameter is given below:

**Conductivity Sensor:** The conductivity sensor must be calibrated according to manufacturer's specifications prior to use in the field against a reference solution that best approximates the ambient conditions that will be measured that day. The sensor is also checked at the end of the sampling day against the same reference standard strength used for calibration.

**Dissolved Oxygen Clark Cell Sensor:** The dissolved oxygen sensor must be calibrated using a water saturated air environment at beginning of the sampling day. During the middle of the sampling run, field teams will check the DO sensor accuracy by placing the unit in a water soaked towel or in the storage cup with a small amount of water to ensure it reads 95% to 105% saturation. At the end of the sample day, the DO sensor is checked for drift by comparing readings to the theoretical saturation point based on barometric pressure and temperature. If the sensor has drifted greater than 0.3 mg/L and less than 0.50 mg/l of theoretical values the probe is serviced before deploying on the next sample run. If the end of day check produces a drift of greater than or equal 0.50 mg/L and verification of the reading shows the error, affected field dissolved oxygen readings are not keyed into CEDS. Large drifts usually indicate improper calibration or a need to change the membrane and electrolyte solution. Winkler titration is the primary method to validate the accuracy of the dissolved oxygen sensor to diagnose sensor performance.

**Dissolved Oxygen Optical Sensor:** Calibration of the optical dissolved oxygen sensor is done using an air saturated water environment at the beginning of the sampling day. A mid day check of the optical sensor is not required. At the end of the sample day, the optical DO sensor is checked for drift by comparing readings to the theoretical saturation point based on barometric pressure and temperature. If the sensor has drifted greater than 0.2 mg/L and less than 0.50 mg/l of theoretical values the probe is serviced before deploying on the next sample run. If the end of day check produces a drift of greater than or equal 0.50 mg/L and verification of the reading shows the error, affected field dissolved oxygen readings are not keyed into CEDS. Large drifts usually indicate improper calibration or damage to the luminescent membrane requiring

maintenance. Winkler titration is the primary method to validate the accuracy of the dissolved oxygen sensor to diagnose sensor performance.

**pH Sensor:** the pH sensor must be calibrated at the beginning of the sampling day using a minimum of two standard buffer solutions that bracket the expected pH of the samples to be measured (e.g. 4.0 & 7.0 or 7.0 & 10.0). Field teams are encouraged to periodically validate the slope of the pH calibration using a third buffer standard (4 or 10) prior to going into the field. The calibration of the sensor must be checked against the same standards used for calibration in the morning. If measurements in the field were outside the bracketed standards used for calibration, the unit is verified with a third buffer (4 or 10) that brackets the observed readings to ensure sensor accuracy. If the sensor has drifted more than  $\pm 0.2$  pH units from the buffer value at the end of day, the validity of the readings should be verified. If verification fails, affected field pH measurements are not keyed into CEDS.

**Temperature Sensor:** The temperature sensor is verified once a year against a NIST certified thermometer using water baths covering a range of temperatures encountered in the field. The instrument and thermometer should agree within  $0.5^{\circ}\text{C}$ . At least six months from the time of the annual verification, regions will compare temperature accuracy by comparing two field units using three water baths which mimic the full range of routinely encountered temperatures. If the units display readings outside  $1.0^{\circ}\text{C}$ , the units are validated with the NIST certified thermometer before taken back out to the field.

**Depth Sensor (pressure transducer):** Depth sensors on multiprobes are calibrated at the sample site prior to deployment at a set depth specified by the manufacturer. This in effect becomes the standard for depth calibration.

### ***B.7.2 Laboratory Operations:***

Calibration of laboratory analytical instrumentation is required to assure the data generated meet data quality objectives. Detailed calibration procedures, calibration frequencies and acceptance criteria are specified in the analytical method SOP. Each laboratory is responsible for the proper calibration and maintenance of laboratory analytical equipment. Calibration activity performance is documented and is available for review during internal and external laboratory audits.

In general, reference standards used “bracket” the expected concentration of the samples. At a minimum, this generally requires the use of three to five different standard concentration levels to quantify the instrument’s linear range. Calibration of instruments must be performed prior to the analysis of samples and then at periodic intervals (continuing calibration) during the sample analyses to verify that the instrument is still calibrated. Sample concentrations outside the instruments linear range need to be diluted and if necessary, reanalyzed.

## **B8 Inspection / Acceptance Requirements for Supplies and Consumables**

This program only utilizes supplies and consumables that are of adequate quality to sustain confidence that the data generated in the sample collection, processing and laboratory analyses will meet the data quality objectives. Where no independent assurance of quality for outside supplies is available, procedures are established to ensure that the quality of the purchased materials is consistent with the overall program technical and quality criteria. Purchased supplies and consumables are not used until they have been inspected, calibrated or otherwise verified to ensure compliance with any relevant standard specifications for use in this program.

### ***B.8.1 Inspection and Acceptance Testing of Supplies and Consumables***

A designated DEQ Environmental Field Specialist Senior inspects chemicals, reagents, bottles, and cubitainers upon arrival. Any broken bottles and containers are shipped back to the manufacturer for replacement.

Laboratory technical staff will be responsible for inspecting incoming equipment and supplies before placing them in service. The manufacturer's specifications for product performance and purity will be used as criteria for acceptance or rejection of supplies and consumables.

### ***B.8.2 Documentation and Tracking of Supplies Consumables***

Records for purchases and receipt of supplies and consumables utilized in the field and laboratory will be maintained at the Regional Offices and contracted laboratory. Return of damaged or inappropriate materials to the suppliers will also be documented.

Documented procedures shall exist at each laboratory for the purchase, receipt, handling/storage and tracking of supplies and consumables to be used for the technical operations. The established procedures must enable program personnel to ensure that supplies and consumables that have not been tested, have expired, or do not meet acceptance criteria are not used for the program.

Each laboratory shall retain records for all the standards, reagents and media including the manufacturer/vendor, the manufacturer's certificate of analysis or purity, the date of receipt, recommended storage conditions and expiration date after which the material shall not be used unless its reliability is verified by the laboratory. The original containers shall be labeled with a unique identifier that links the containers to the aforementioned records and include the date the container was opened.

## **B9 Non-direct Measurement**

Data will primarily be generated through WMA field activities and consequent laboratory analyses. If data from sources other than VADEQ will be utilized for VADEQ purposes, the outside source and their contracting laboratories must have a Quality Assurance Project Plan reviewed and approved by the DEQ Quality Assurance Coordinator for that use. Laboratory

analysis performed by outside data sources must be certified complaint under the Virginia Environmental Laboratory Accreditation Program (VELAP) or applicable authority.

## **B10 Data Management**

### ***B.10.1 Data Recording***

Field observations and records such as sample collection information will primarily be recorded manually using a field data sheet. All field data sheets will be filed at the Regional Office generating the data. Validated field data will be entered into the CEDS database at the end of sampling day. The CEDS database has a range check system built into the data entry screen. Values exceeding the programmed maximum for a given field parameter are automatically removed from the screen and an error message is generated to inform the field specialist that an invalid value had been entered.

### ***B.10.2 Data Validation***

The data validation process is described in section D2 of this QAPP.

### ***B.10.3 Data Transformation***

Data transformation is expected to consist of transferring test results from one unit of measure to another (i.e. mg/kg to µg/kg). Transformation will be automated within the database to prevent transcription errors and the number of significant figures reported will be sufficient to prevent rounded or truncated results.

### ***B.10.4 Data Transmittal***

The laboratory's electronic data files are loaded into the CEDS database via an automated File Transfer Protocol (FTP). Once the files have been processed by the system, they are archived on the server to retain the original data files.

### ***B.10.5 Data Reduction***

Data reduction is addressed in Section D.1.

### ***B.10.6 Data Analysis***

WMA staff at Central Office will perform data analysis of field and laboratory data. The appropriate statistical methods will be used to analyze data.

### ***B.10.7 Data Tracking***

The flow of data through the system includes loading, verification, and validation. The current system of data tracking is as follows:

Analytical files produced by DCLS are placed on their FTP site. The files are obtained daily by VADEQ and loaded into the CEDS database via an automated program. An automated notification process informs specified personnel at DCLS when the files are downloaded by VADEQ. If no notice is generated, DCLS personnel notify VADEQ technical personnel that the download program did not perform properly. If, during the upload to the CEDS database an error occurs, an automated error message is generated and e-mailed to VADEQ technical personnel who then track down the source of the error. An additional program checks the analytical data for completeness of parameters during the upload and an error report is written to the database that can be accessed by all VADEQ personnel in the report module.

VADEQ also generates files for DCLS twice daily containing the field data and sample containers collected on the previous sampling day and the analytical services required for each sample container. An additional file is generated from the monthly run data module of CEDS to give the analytical chemists an idea of services that will be requested such that they can be sure to have the available reagents and bacterial media available on a given day.

Each data record in the CEDS database is date/time stamped when it is downloaded to a file generated for DCLS. VADEQ personnel check the CEDS database daily to ensure all samples collected in the field on the previous day have been processed by the system. Additionally, samples analysis requests as scheduled in CEDS are output to a report by the DCLS LIMS database and manually checked in central receiving against each container received by the lab. DCLS then notify the VADEQ Laboratory Liaison when samples are received without the accompanying electronic information or if they have received electronic information for samples not sent to the lab.

### ***B.10.8 Data Storage and Retrieval***

The information management system is a commercially available client/server based relational database system allowing connections of multiple users. An Oracle 10g database provides a central repository for all the data. Multiple users can connect to the system from their workstations over the internet via a web interface. Basic workstation requirements are:

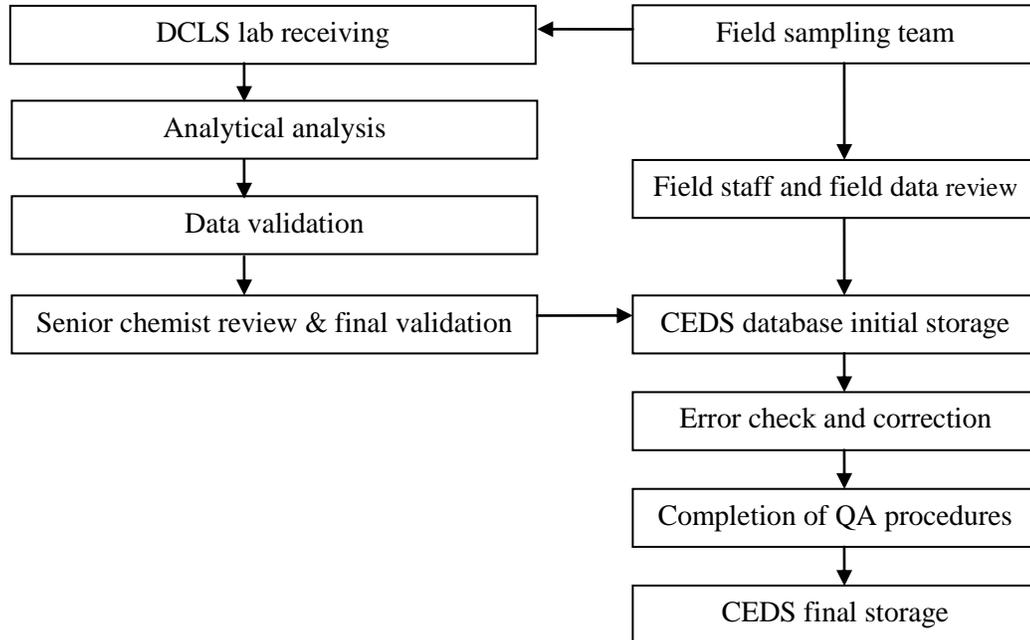
- Pentium II 200MHz or faster PC
- 512MB RAM, 1.5 GB of free hard disk space
- Windows NT/2000/XP

The data management system is highly secure with firewall protection and multiple layers of user authentication. Within the system itself, security administration allows users to be assigned to a group with various permissions controlling what each user can access. User access to data in the database, reports, table administration, and many other features are all controlled. The database manager is required to provide a list of approved users for the system and define user groups with associated security levels. In addition, backups of the database are run daily to ensure data preservation. Backups of the data will be retained in a secure and safe office.

Retrieval of the data can be accomplished through the web interface. Approved users can download the data to their computers for use in a spreadsheet, run customized reports, process customized queries, or simply review the data through an explore like window.

Figure 4 illustrates the data flow from measurement in the field to final use and storage.

**Figure 3. Data Flow**



## **C1 Assessments and Response Actions**

Performance and system audits of both field and laboratory activities will be conducted to verify that sampling and analysis are performed in accordance with the procedures established in the SOP and QAPP.

### ***C.1.1 Audits of Data Quality***

Field blank and field duplicate data will be reviewed in order to assess the quality of sampling activities.

Analytical and measurement data should be reviewed in order to assess the quality of measurement and analytical activities, respectively.

Metadata should be reviewed in order to assess precision and accuracy.

The WMA Quality Assurance Coordinator has the ultimate responsibility to accept or reject data.

### ***C.1.2 Technical Systems Audits***

#### **C.1.2.1 Field Sampling Audits**

Field sampling audits evaluate field operations in comparison to the written procedures outlined in SOPs and other requirements established in the project plan and WMA SOP. The WMA QA Coordinator, or designated staff member, will conduct field sampling audits at least once a year. Additional audits will be scheduled if warranted by the initial audit observations and findings. The primary audit elements for the program are:

- Availability, appropriateness and use of field SOPs.
- Sampling methodology
- Sample handling procedures
- QA procedures
- Field instrument operation logbook
- Field maintenance logbooks
- Field documentation
- Field data quality, quantity and timeliness
- Follow-up on previous corrective action and recommendations

The WMA QA Coordinator will prepare, or review and approve the audit report prepared by the designated staff member, which discusses deficiencies found during the on-site evaluation with recommendations for corrective action. The report will be forwarded to the regional water quality monitoring program managers.

#### **C.1.2.2 Laboratory Performance and Systems Audits**

Internal and external audits are conducted regularly at DCLS to monitor the overall effectiveness of the quality assurance system. The DCLS QA Officer of that specific lab performs internal audits. They are responsible for all QA/QC functions in the laboratory, and/or members of the professional laboratory staff that do not normally work in the section or analytical unit being audited. Non direct employees of DCLS perform external audits are in order to provide an independent and unbiased review of laboratory operation.

There are two types of audits: system audits and performance audits. 1) System audits involve an in-depth review and evaluation of some or all of the components of the analytical laboratory to determine if guidelines listed in the QA plans are properly applied. 2) Performance audits require the analysis of blind samples or other samples whose values are not known to the analytical lab. These results are used to evaluate the accuracy of the lab analytical system.

#### 1) Internal Audits

The QA Officers conduct several system audits each calendar year. During these audits, one or more components of lab are reviewed to determine if that part is functioning in compliance with the DCLS Quality Manual, the approved standard operating procedures and approved methodology. An audit report includes a list of deficiencies that must be addressed in order to correct or improve the lab operations.

System components to be audited during the internal audit include, but are not limited to:

- All documentation associated with sample and data handling, to include linkage mechanism employed between all records for tracking documentation for any sample data result.
- Use of established approved procedures as outlined in the Quality Manual.
- Personnel training records
- Proper execution of established procedures.
- Follow-up to corrective actions from previous audits.
- Sample and data handling activities: all sample login, routing and disposal; sample preparations; method calibrations; sample analyses; data reduction, validation and reporting; preventative maintenance and repair procedures; standard and reagent preparation, documentation and storage; sample and waste disposal; container and labware decontamination; QC management practices and assessment of analytical precision, accuracy and sensitivity.
- Deficiency lists and associated corrective action orders are formally communicated to responsible staff.

#### 2) External Audits

External audits are performed when certifying agencies conduct on-site inspections. USEPA, NELAC, or other certifying authority conducts external laboratory systems and performance audits.

### C.1.2.3 Performance Audits

The laboratory is involved in external performance audits conducted through the analysis of performance evaluation samples provided by the QA Officers or a third party provider. These audits consist of performance sample audits and blind sample audits.

#### 1) Performance Sample Audits

Performance sample audits are conducted periodically by the DCLS QA Officers and VADEQ using commercially prepared samples as blind samples. The results of these audits are documented and reported to managers so that any necessary adjustments can be made.

#### 2) Blind Sample Audits

Blind sample audits are performed by submitting QC samples to the analyst. The true values are only made known after the test is completed. Blind sample audits are carried out by the DCLS QA Officers, VADEQ, and certifying agencies as necessary to assure the lab is capable of achieving success with a blind QC sample.

### **C.1.4 Corrective Action**

The first level of responsibility for identifying the need for corrective action is with field and laboratory technical staff during routine sampling and analysis activities. The second level of responsibility is with any person observing deviations during field audits, while reviewing field documentation, or while reviewing laboratory results.

Each time the need for corrective action is identified, the problem and steps taken to resolve it are documented on the corrective action request and tracking form used by VADEQ (Appendix C), or similar variant. This form documents the problem, the recommended corrective action, mechanism of implementing the corrective action and responsible personnel.

#### C.1.4.1 Field Corrective Action

Corrective actions will be initiated if the field team is not adhering to the prescribed sampling or documented procedures or if laboratory analyses are experiencing interference or systematic contamination due to field sampling procedures or sample handling protocol. Corrective actions begin with identifying the source of the problem. Corrective action responses may include more intensive staff training, modification of field procedures, or removal of the source of systematic contamination. Once resolved, the corrective action procedure will be fully documented.

#### C.1.4.2 Laboratory Corrective Action

Problems should be resolved at lowest level possible. When quality assurance data exceed a threshold of acceptable limits corrective action should be taken immediately and all actions documented. Laboratory staff notifies supervisors when unsure of the appropriate corrective

action. The group manager, senior chemists, principal, QA Officer, QA Manager and laboratory administration review all corrective actions. The QA committee member will compile quality assurance data and corrective actions in monthly summaries and submit it to the QA Officers on a monthly basis. The QA Officers provide recommendations and continue to monitor to ensure detected problems are resolved. If the initial corrective action fails to resolve the problem or a trend is established, the QA Officer may make additional recommendations or establish an action team to seek a resolution. The goal of the laboratory is to detect problems early, implement changes to improve services, and monitor for effect.

## **C2 Reports to Management**

The WMA QA Coordinator will prepare QA reports to VADEQ management and regional program managers on a quarterly basis.

Each report will address the following topic areas:

- Results of performance and system and field audits.
- Evaluation of compliance with QA project plan.
- Evaluation of data quality measurement trends.
- Identification of QA problems, program needs and recommendations for solutions.

The WMA QA Coordinator will prepare an annual Quality Assurance report. The quality assurance report will summarize the results of QA/QC assessments and evaluations, including precision, accuracy, comparability, representativeness and completeness of the monitoring data; will provide a summary of the field split and equipment blank analyses and will provide a summary of any lab and/or field performance audits that were conducted. The annual report will be distributed to the program managers and management.

## **D1 Data Review, Validation, and Verification**

The field, laboratory and data management activities described in this QAPP will be reviewed to assess whether these activities were performed in a manner that is appropriate for accomplishing the program objectives. This assessment will include electronic verification of the data and data validation. Data verification is confirmation by examination and provision of objective evidence that specified requirements have been fulfilled. Data verification concerns the process of examining a result of a given activity to determine conformance to the stated requirements for that activity. Data validation is confirmation by examination and provision of objective evidence that specified requirements have been fulfilled. Data validation concerns the process of examining a product or result to determine conformance to the user needs.

### ***D.1.1 Review of Sampling Design***

The ability of the collected samples to conform to sampling design specifications in section B1 of the QAPP will be reviewed by the WMA QA Coordinator. Those samples that deviate from the sample design and may impact program objectives, if any, will be discussed in the monthly water monitoring and assessment conference call.

### ***D.1.2 Review of Sample Collection Procedures***

The sample collection procedures will be reviewed to confirm that samples are collected in accordance with section B2 of this QAPP. The review will note unacceptable departures, if any from the sample collection methods outlined in the WMA SOP and identify sample data (analytical or field) that should be excluded from incorporation into the database.

To assure that all field data are collected accurately and correctly, field audits as described in section C1 will be performed during sample collection to document that appropriate procedures are being followed with respect to sample collection. These audits will include a thorough review of information related to sample collection.

The data review of equipment blanks and other field QC samples will provide definitive indications of the data quality. If the data indicate a problem exists in the sampling or analytical procedures, the problem can be quickly isolated via the complete sample tracking and documentation procedures that are performed. If such a problem does arise, corrective action can be instituted and documented. If there is compromised data due to a problem, the appropriate data qualifications will be used to identify the data.

### ***D.1.3 Review of Sample Handling***

The labeling and identification of samples will also be reviewed to ensure samples properly represent the location they were intended to represent. It is expected that labeling errors will be minimal due to use of preprinted labeling and checks in the database.

The handling, preservation and storage of samples collected during the sampling will be monitored on an on-going basis. The field audits described in section C1 will provide documentation on proper handling of samples during collection and processing. The WMA Managers will review these audits to determine if sample representativeness was maintained during collection and processing. Additionally, laboratories will document sample receipt including proper containers and preservation. Any deviations from the accepted practices will be provided to the DEQ Laboratory Liaison who will notify the appropriate regional personnel for action. Data identified as having sample handling, storage or preservation problems will be qualified to warn the data users of possible data quality deficiencies.

#### ***D.1.4 Review of Analytical Procedures***

The use of proper analytical procedures described in section B4 of this QAPP will be reviewed primarily through the data verification and validation methods discussed in section D2. Qualification of data that does not conform to criteria is also discussed in section D2.

The DEQ Laboratory Liaison will review the analytical requests scheduled in the database and parameter completeness reports to confirm that samples were tested using the correct analysis methods. The review will determine if samples submitted for analysis actually had the analyses performed. If the analyses that were identified to be performed were not actually performed (due to loss of sample, lab error etc.) then a determination should have been made at the time the missing data was discovered and appropriate corrective action documented.

#### ***D.1.5 Review of Quality Control***

The review of quality control checks described in section B5 of this QAPP will be conducted primarily through the data verification and validation methods discussed in section D2. Qualification of data that does not conform to criteria is also discussed in section D2.

#### ***D.1.6 Review of Calibration***

The review of quality control checks described in section B7 of this QAPP will be conducted primarily through data verification and validation methods discussed in section D2. Qualification of data that does not conform to criteria is also discussed in section D2.

The regional water quality monitoring managers will review field equipment calibrations and identify any impacts to non-analytical data that may exist.

### ***D. 1.7 Data Reduction and Processing***

Data generated through field activities and laboratory operations shall be reduced and validated.

#### ***D.1.7.1 Field Data Reduction***

Field data will be recorded manually on a field data sheet at the time of measurement. These data include date and time collected, station ID, weather, tide or flow, measurements of

temperature, dissolved oxygen, pH, conductivity, and the collector's initials. If errors are made on the field data sheet, results will be legibly crossed out, initialed by the person making the correction, and corrected in a space adjacent to the original entry. The field data will then be entered into CEDS database at the end of sampling day. To minimize transcription errors and make sure the field data and analytical requests were properly saved, field staff should save their work, query the information back into the screen and proofread the values displayed on the screen.

#### D.1.7.2 Laboratory Data Reduction

The laboratory's goal is to minimize the steps needed to transform raw data into reportable results and maximize on the number of analytical results generated by automated systems. The more automated the data reduction process, the less likely data transcription and calculation errors are to occur.

Laboratory data reduction procedures are discussed in detail in each laboratory QA manual.

## D2 Validation and Verification Methods

The data verification and validation process is designed to ensure that transcription and data reduction errors are minimized, a full and complete data collection record exists and can be produced on demand, the data are actually reviewed, that all variances which affect the data are noted and qualified, and most importantly that any variances or issues which may result in loss of use of data are documented and corrected.

### ***D.2.1 Data Verification:***

Data verification uses a documented systematic set of assessment requirements, to ensure the data set meets a specified set of criteria as described in the QAPP. Personnel who collected the data perform verification of the data before validating. Supervisors spot check the data to ensure accuracy. This systematic process evaluates data collection performance and compliance against a set of standards for completeness, correctness and consistency.

Field data verification activities include field audits to ensure the following:

- 1) The applicable SOPs are followed for sample collection
- 2) The required number of blanks and splits are collected
- 3) The field instruments have been calibrated according to the SOPs and documented in the logbook
- 4) Sample integrity is preserved (sample preservation and handling), and
- 5) Internal checks are followed to ensure correct data entry.

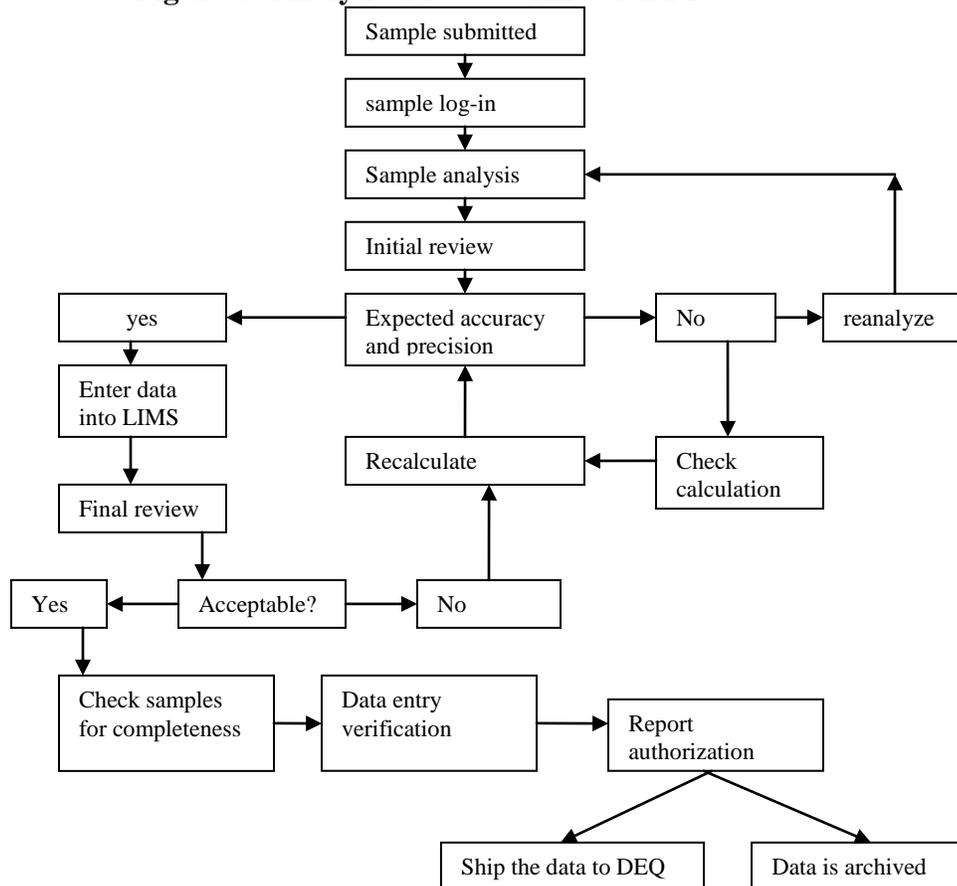
Figure 5 is shows a flow chart of the analytical data verification process. Data verification is the routine laboratory process through which proper quantification, recording, transcription, and calculations are confirmed. It also confirms that the data is reasonable and complete. The process

should be such that errors are minimized and that corrective action steps are taken and documented when errors are detected. The objective of data verification is to provide results of verifiable and acceptable quality whose validity is not jeopardized. The data verification process ensures that:

- The correct samples are reported;
- There were not systematic errors in calculating final results;
- Samples were analyzed within calibration and required holding times;
- The quality control elements monitored were within known acceptance limits.

Each analyst and/or technician is responsible for ensuring that the results of each analytical determination have all associated QC measurements (completeness) and that the acceptance criteria are met and documented according to the protocol (correctness). The analyst and/or technicians is responsible for checking calculations, completing sample preparation, calibration, analysis, standard and instrument logs. The Senior Chemist is responsible for reviewing this work for completeness and correctness prior to authorizing the individual results for release. This includes checking for appropriate flagging of final results. Any discrepancy will initiate a recheck of data or reanalysis of the samples.

**Figure 4. Analytical Data Verification Processes**



### **D.2.2 Data Validation:**

Data validation is a process of verifying that qualitative and quantitative information generated relative to a given sample is complete and accurate. Data validation process shall be performed for both field and laboratory operations as described below:

#### **D.2.2.1 Field Data Validation Process**

Processes to evaluate field data for this program primarily include reviewing field data sheets to check for transcription errors by the field staff and field quality control data. These procedures are performed to ensure that field measurements were properly performed and documented. The field data documents includes data generated during measurement of field parameters, observations, results of any quality control sample analyses, and field instrument calibrations. This task will be the responsibility of WMA QA Coordinator who will not participate in making any of the field measurements.

The number and type of field QC samples should comply with program objectives. Field QC samples provide information to the data validator about sampling conditions, sampling techniques, field precision and sample homogeneity. The data validator confirms that field QC samples were sent to the laboratory at the required frequency.

#### **D.2.2.2 Laboratory Data Validation Process**

1. Review the data and all the information associated with its collection to be sure that all required documents and form were filled out correctly and completely.
2. Verify that all field quality control samples were taken at the frequency specified by the program DQOs and submitted for analysis.
3. Laboratory quality control objectives were met and both results are included. Items to be verified include holding times, sample preservation and storage, sampling techniques, QC sample results (duplicates, spikes, blanks).
4. Examine the raw data and verify calculations and transfer accuracy of about 10% of all raw data unless errors are found. If errors are identified, another 10% of the raw data must be examined.
5. Examine the raw data for very high or very low values, or unexpected values which may result for misplaced decimal points, transcription errors, rounding error or instrumentation malfunction.

Data qualifier codes will be applied to those sample results that fall outside of QC acceptance criteria. An explanation of data qualifier codes is provided in Appendix D.

CEDS database has been programmed with the capability to screen the data. The automated screening process occurs during data entry and analytical data uploads validating field data entry, analytical results, and QC sample results by identifying outliers based on the acceptable limits. Data failing to meet the criteria are flagged in a valid value field and/or

written to an error report to alert the data users. The data users should validate the data before the data is assessed (see Figure 6)

#### D.2.2.3 Data Entry Screen

Initial entry of sampling information and field data into the VADEQ computer system must meet field specific criteria. The data entry screen has built in checks for valid station identifications, sampling run ID, laboratory service requests, collector's initials, and range checks for field measurements.

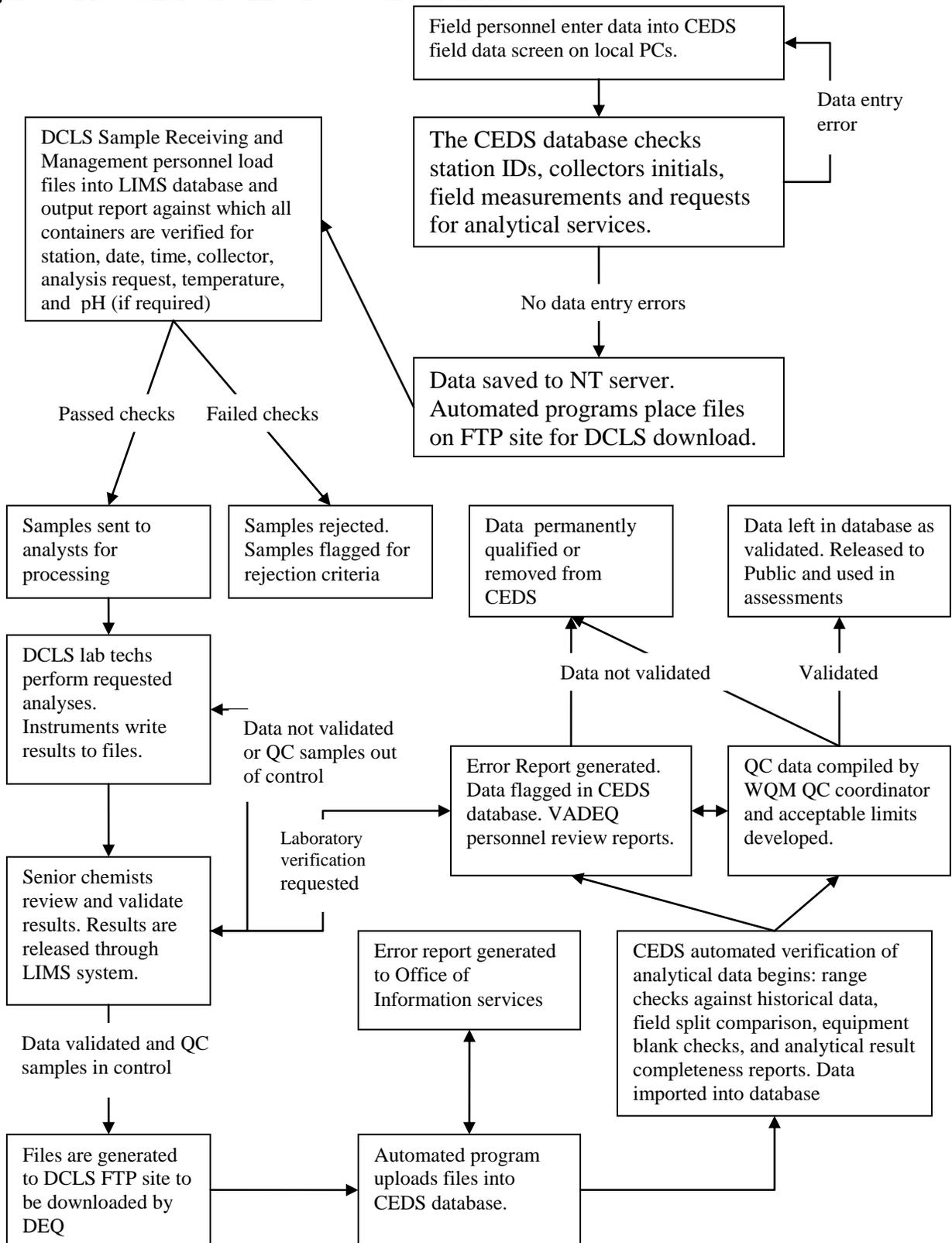
#### D.2.2.4 Analytical Data Screen

Data limits for this initial screening have been established for each parameter based upon analytical reporting limits. These limits are used to identify outliers and data, which are within the described detection limit for each parameter. Upper limits have been set for those parameters such as pH analyses where analytical methods define an upper detection limit. In addition, a "parts < whole" check is performed on the data where fractions and total parameter determinations are made, such as for solids analyses.

#### D.2.2.5 Historical Data Range Checks

For the historical screening, parameter limits have been established using historical ambient data. Each analytical result is compared to a historical high and low criteria based on all the historical values available for the sample collection site, depth and month of collection. When a site has less than 12 samples collections, the values are compared to high and low generic values for the analyte based on the entire available data set for that parameter. Ranges of data variation will be further demarcated using relevant geographic and environmental considerations and appropriate statistical analysis. Any data outside of the historical ranges are flagged as invalid in the database and written to an error report that is available to all VADEQ personnel.

**Figure 5. Flow Chart of CEDS Data Validation Process**



#### D.2.2.6 Quality Control Sample Screening

For key parameters of interest, 4% of the total annual station samples submitted to DCLS will be quality control samples (equipment blanks and field splits). Results from these quality control samples will be used to establish control limits for the validation system. VADEQ implemented system of generating QC samples in 1999. Because of the volume of data generated since that time, a program has not yet been developed in CEDS to validate these data in their entirety. Currently the CEDS database compares replicate results against each other to ensure they are within 5% of each other. Equipment blank results are compared to the analytical MDLs reported by DCLS to produce an error report for any values that exceed the analytical MDL. The WMA QA coordinator periodically reviews these reports and provides a summary of the findings to the regional WMA managers who are then required to review and request laboratory verifications if necessary and give a response to the WMA QA coordinator on their findings as appropriate. Data in the database are then flagged, removed or validated based on the response.

As an additional QC check, the WMA QA coordinator utilizes statistical analyses to develop an acceptable range of parameter variation for field blanks and field splits based on the range of results for the entire agency. For split samples, the precision can be expected to vary with concentration. Results are reviewed for the presence of developing trends which may be indicative of procedural error. If the presence of a trend is detected the affected region is notified and a corrective action is implemented to find and eliminate the source of error.

### D3 Reconciliation with User Requirements

Samples collected and correctly analyzed will subsequently be assessed for possible inclusion in the Integrated 303(d)/305(b) Report, TMDL development, permit decisions or other purposes. One of the main objectives of WMA is to use the generated data to determine the percentage of stream segments with water quality standard violations. If the data from a sampling station shows an exceedance of applicable water quality standards for the conventional pollutants in more than 10.5% of the samples collected, the segment may be subjected to impairment listing for the identified pollutant(s). Additional information can be found in the 2010 WQA Guidance Manual available at [www.deq.virginia.gov/wqa/guidance10.html](http://www.deq.virginia.gov/wqa/guidance10.html).

In general, WMA data rejected during laboratory analysis or during the data validation process are not quality assured and thus not considered for assessment. However, other qualified data not meeting QA/QC requirements may be used for listing or delisting waters on the 303(d)/305(b) list or for TMDL development on a case by case basis provided the potential uncertainties associated with the data are addressed and the appropriate caveats are documented.

# Appendices

**Appendix A: Target Analyte List and Method Detection Limit**

**Polychlorinated Biphenyls (EI)**

ANALYTE	MDL (ng/kg)	ANALYTE	MDL (ng/kg)
PCB-1	12	PCB-67	15
PCB-10/4	16	PCB-7/9	39
PCB-101	10	PCB-70	18
PCB-119	14	PCB-71	31
PCB-121	8	PCB-72/64/41	31
PCB-13	12	PCB-76	23
PCB-136	18	PCB-84	12
PCB-15	13	PCB-89	17
PCB-16	32	PCB-91	11
PCB-17	5	PCB-92	22
PCB-18	8	PCB-94	19
PCB-19	13	PCB-98/102	29
PCB-22	18	PCB-99	12
PCB-25	11		
PCB-26	15		
PCB-27/24	14		
PCB-29	10		
PCB-3	15		
PCB-30	8		
PCB-31	15		
PCB-33/20	19		
PCB-34	13		
PCB-37	27		
PCB-40	20		
PCB-43	47		
PCB-44	13		
PCB-45	34		
PCB-46	26		
PCB-48/47/75	48		
PCB-49	18		
PCB-5/8	16		
PCB-51	16		
PCB-52	11		
PCB-53	10		
PCB-55	13		
PCB-56/60	15		
PCB-59/42	22		
PCB-6	27		
PCB-63	18		
PCB-66	15		

**Polychlorinated Biphenyls (NCI)**

ANALYTE	MDL (ng/kg)	ANALYTE	MDL (ng/kg)
PCB-105	29	PCB-200	24
PCB-111/87/115	50	PCB-201	28
PCB-118	27	PCB-202	27
PCB-120/110/85	37	PCB-203/196	33
PCB-125/116	46	PCB-206	23
PCB-128	20	PCB-77	46
PCB-129	19	PCB-82	23
PCB-130	24	PCB-83	28
PCB-131/146	36	PCB-97/86	93
PCB-133	21		
PCB-134	23		
PCB-135/144	33		
PCB-137	20		
PCB-138/158	40		
PCB-139	36		
PCB-141	21		
PCB-149	36		
PCB-151	18		
PCB-153/132	117		
PCB-156	34		
PCB-157	40		
PCB-163/164	51		
PCB-167	25		
PCB-170/190	49		
PCB-171	43		
PCB-172	27		
PCB-174	21		
PCB-175	22		
PCB-176	20		
PCB-177	45		
PCB-178	18		
PCB-179	18		
PCB-180/193	54		
PCB-183	19		
PCB-185	19		
PCB-187	21		
PCB-191	27		
PCB-194	22		
PCB-195	19		
PCB-199	14		

### Organochlorine Pesticides

<u>Compounds</u>	<u>MDL(ug/kg)</u>
a-Chlordane	0.87
Aldrin	1.23
a-Lindane	1.40
b-Lindane	1.43
Chlorbenzilate	1.03
Di-Allate	1.98
DiBromoChloroPropane	1.60
Dieldrin	1.40
d-Lindane	0.99
Endosulfan	0.95
Endosulfan II	1.53
Endosulfan Sulfate	1.13
Endrin	1.69
Endrin Aldehyde	0.61
Endrin Ketone	0.99
g-Chlordane	0.95
g-Lindane	0.99
Heptachlor	1.98
Heptachlor Epoxide	0.95
Hexachlorobenzene	1.03
Hexachlorocyclopentadiene	2.56
Isodrin	1.26
Kepone	1.90
Methoxychlor	1.69
p,p'-DDD	0.95
p,p'-DDE	0.95
p,p'-DDT	1.88

### Organophosphorous Pesticides

<u>ANALYTE</u>	<u>MDL (ug/kg)</u>
Aspon	0.48
Bolstar	1.74
Carbophenothion	0.95
Chlorfenvinphos	0.95
Chlorpyrifos	0.67
Coumaphos	0.73
Crotoxyphos	0.61
Demeton (Metasystox)	2.56
Diazinon (Dimpylate)	0.48
Dichlorofenthion	0.67
Dichlorvos	1.84
Dicrotophos	1.40
Dimethoate	2.14
Dioxathion	1.69
Disulfoton	1.60
EPN	0.87
Ethion	1.90
Ethoprop	1.13
Ethyl Guthion	0.95
Famophos	0.95
Fenitrothion	0.67
Fensulfothion	1.23
Fenthion	0.73
Folex (Merphos)	2.05
Fonofos	0.95
Guthion	1.43
Leptophos	0.95
Malathion	0.61
Methyl Chlorpyrifos	1.03
Methyl parathion	1.74
Mevinphos	1.53
Monocrotophos	0.99
Parathion	0.73
Phorate	0.87
Phosmet	0.87
Phosphamidon	0.61
Ronnel	0.95
Stirophos (Tetrachlorvinphos)	0.87
Sulfotep	0.87
Terbufos	0.95
Thionazin	1.74
Tokuthion	0.67
Trichlornate	0.48

### Chlorinated Herbicides

<u>Compounds</u>	<u>MDL(ug/kg)</u>
Dalapon	*
3,5 Dichlorobenzoic Acid	3.61
4-Nitroanisole	3.00
Dicamba	2.74
MCPP	2.53
MCPA	3.27
Dichloroprop	3.09
2,4-D	1.58
Pentachloroanisole	3.51
Silvex	2.90
Chloramben	3.27
2,4,5- T	2.36
2,4-DB	6.08
Dinoseb	3.03
Bentazon	2.48
Pichloram	2.00
Dacthal	*
Acifluorfen	2.24

\* - Compounds only screened for due to poor recovery as per DEQ sediment QAPP

### Polyaromatic Hydrocarbon

<u>Compounds</u>	<u>MDL (ug/kg)</u>
1,4-Dimethylnaphthalene	7.7
1-Methylfluorene	6.5
1-Methylnaphthalene	8.1
1-Methylphenanthrene	5.8
2,3,5-Trimethylnaphthalene	7
2,6-Dimethylnaphthalene	7.5
2-Methylantracene	5.8
2-Methylnaphthalene	8.1
2-Methylphenanthrene	6.1
3,6-Dimethylphenanthracene	5.7
9,10-Dimethylantracene	4.1
9-Methylantracene	6.9
Acenaphthalene	7.4
Acenaphthene	5.4
Anthracene	4.5
Benzo(e)pyrene	7.4
Benzo[a]anthracene	4.6
Benzo[a]pyrene	2.6
Benzo[b]fluoranthene	7.2
Benzo[g,h,i]perylene	5.9
Benzo[k]fluoranthene	7.0
Biphenyl	8.1
Bis(2-ethylhexyl)phthalate	19.9
Butylbenzylphthalate	24.9
Chrysene	3.7
Dibenzo[a,h]anthracene	6.3
Diethylphthalate	7
Dimethylphthalate	6.6
Di-N-Butylphthalate	22.8
Di-N-Octylphthalate	11.8
Fluoranthene	5.4
Fluorene	6.9
Indeno[1,2,3-C,D]pyrene	5.9
Naphthalene	7.6
Perylene	4.9
Phenanthrene	6.5
Pyrene	4.7
Triphenylene	6.8

## **Appendix B**

**VA DEQ WMA Program Standard Operating Procedures (Separate Document)**

**Appendix C: Corrective Action Request (CAR) Form**

Corrective Action Request Form

Section I: to be completed by originator

Submitted by: \_\_\_\_\_ Date: \_\_\_\_\_

A. Nature of Problem:

B. Possible Cause:

C. Date of Problem Identified: \_\_\_\_\_

D. Samples That May Be Invalid:

E. Recommended Corrective Action (Optional):

Continued on next page

**Corrective Action Request Form- Continued**

Section II: to be completed by program manager

Name: \_\_\_\_\_ Date: \_\_\_\_\_

A. Recommended Corrective Action:

B. Follow Up Action Required:

C. Implementation Will Begin On:

Section III: to be completed by QA Officer

Name: \_\_\_\_\_ Date: \_\_\_\_\_

A. Recommended Corrective Action:

B. Follow Up Action Required:

C. Implementation Will Begin On:

#### Appendix D: Data Qualifier Codes

Code	Description
\$	Calculated by retrieval software. Numerical value was neither measured nor reported to the database, but was calculated from other data available during generation of the retrieval report.
<	Value less than the number reported.
>	Value greater than the number reported but unknown.
A	Value is the mean of two or more determinations.
B	Results based upon colony counts outside acceptable range.
C	Calculated. Value stored not measured directly.
CAB	Algal bloom, no sample taken.
CAS	Algal sample taken.
CBF	Biofouling.
CDB	Disturbed bottom.
CFK	Fish kill.
CLF	Low flow.
CMS	Confirmed by Mass Spec.
CSC	Site location change.
CSW	Salinity level calibrated incorrectly.
CTC	Time change.
CTF	Temperature probe failure.
CTS	Time skip.
CTW	Turbid water.
CWD	Instrument at wrong depth.
D	Field measurement.
E	Extra sample taken in compositing process.
F	In the case of species, F indicates female.
FO	Value is not valid.
G	Value is the maximum of the two or more determinations.
GBO	Blocked optic.
GNV	Negative value.
GPC	Post calibration out of range.
GPF	Probe failure.
GSC	Seal compromise.
GWL	Wiper lost.
GWM	Wiper malfunction.
H	Value based on field kit determination; may not be accurate.
I	STORET CONVERSION
IF	Possible analyte interference not confirmed as substance.
J	Estimated. Value is not result of analytical measurement.
JB	Compound was found in the blank and sample. Result is < the RL but > or = to MDL.
K	Off-scale low. Actual value not known, may indicate failure to detect substance.
L	Off-scale high. Actual value not known, but known to be greater than value shown.
LB	Calibration drift for both the LI-COR underwater and LI-COR air sensor is greater than or equal to 10% each since their purchase or most recent recalibration.
LQ	Off-scale high. Actual value not known, but known to be greater than value shown. Sample processed beyond holding time.
LS	Calibration drift for LI-COR deck sensor is greater than or equal to 10% since its purchase or most recent recalibration.

Code	Description
LU	Calibration drift for LI-COR underwater sensor is greater than or equal to 10% since its purchase or most recent recalibration.
M	Presence of material verified, but not quantified. Indicates a positive detection, at a level too low to permit accurate quantification. In the case of temperature or oxygen reduction potential, M indicates a negative value. In the case of species, M indicates male sex.
MD	Less than the MDL as calculated by 40CFR136.
MT	Presence of material verified, but not quantified. Value reported is less than the criteria of detection.
N	Presumptive evidence of presence of material.
NIR	Instrument removed.
NIS	Incorrect instrument setup. QUALITY CONTROL FAILURE. DATA NOT VALID.
NJ	The analysis indicates the presence of an analyte that has been tentatively identified and the associated numerical value represents its approximate concentration.
NND	No data.
NNF	Ram clogged, no flow.
NOW	Instrument out of water.
NPF	Power failure.
NQR	Data rejected due to QA.
O	Sampled for, but analysis lost. Accompanying value is not meaningful for analysis.
P	Too numerous to count.
PDP	DO poisoning (anoxia).
PSW	Salinity calibrated to incorrect level.
Q	Sample held beyond normal holding time.
QF	QUALITY CONTROL FAILURE. DATA NOT VALID.
QFQ	Quality control failure. Sample analyzed beyond holding time.
QQ	Analyte detected above the MDL but below the method quantification limit.
QQQ	Sample beyond hold time. Analyte detected above MDL below RL.
QT	Sample held beyond normal holding time, value reported is less than the criteria of detection.
QU	Sample held beyond normal holding time, material was analyzed for, but not detected. Value stored is the limit of detection for the process in use.
R	Significant rain in the past 48 hours.
RR	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
S	Laboratory test.
T	Value reported is less than the criteria of detection.
U	Material analyzed for, but not detected. Value stored is the limit of detection for the process in use. In the case of species, undetermined sex.
UJ	The analyte was not detected above the reported sample quantification limit. However, the reported quantification limit is approximate and may or may not represent the actual limit of quantification necessary to accurately and precisely measure the analyte in the sample.
UQ	Sample held beyond normal holding time, material was analyzed for, but not detected. Value stored is the limit of detection for the process in use.
UQF	Value reported is less than the criteria of detection. QUALITY CONTROL FAILURE. DATA NOT VALID.
V	Indicates the analyte was detected in both the sample and associated method blank.
W	Value observed is less than the lowest value reportable under remark "T".
X	Value is QUASI vertically-integrated sample.
Z	Too many colonies to count (TNTC), the numeric value represents the filtration volume.