Quality Assurance Project Plan and Sampling and Analysis Plan

Water Quality Program

Denver Department of Environmental Health
Division of Environmental Quality

Revision 3.0

January 1, 2015

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List of Acronyms

APHA	American Public Health Association
BMP	Best Management Practice
CCoD	City and County of Denver
CDPHE	Colorado Department of Public Health and Environment
CDWR	Colorado Division of Water Resources
COC	Chain of Custody
DEH	Denver Department of Environmental Health
Diss	Dissolved
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
EPA	US Environmental Protection Agency
EQD	DEH Environmental Quality Division
FSTM	Field Sampling Team Member
GIS	Geographic Information System
GPS	Global Positioning System
ID	Identification
LCS	Laboratory Control Sample
MCM log	Meter Calibration and Maintenance Log
MS	Matrix Spike
MS4	Municipal Separate Storm and Sanitary Sewer
NAD	North American Datum
NIST	National Institute of Standards and Technology
NIWA	National Institute of Water and Atmospheric Research
PAH	Poly Aromatic Hydrocarbons
PD	Potentially Dissolved
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
%R	Percent Recovery
RPD	Relative Percent Difference
SA	Spiked Amount
SOP	Standard Operating Procedure
Sp Cond	Specific Conductivity
SP CURE	South Platte Coalition for Urban River Evaluation
SR	Sample Result
SSR	Spiked Sample Concentration
SVOC	Semivolatile Organic Compounds
TDS	Total Dissolved Solids
Temp	Temperature
TKN	Total Kjeldahl Nitrogen
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
Tot	Total
TSS	Total Suspended Solids
TREC	Total Recoverable
USGS	US Geological Survey
VOC	Volatile Organic Compounds
WMD	Wastewater Management Division
WQCC	Water Quality Control Commission
WQCD	Water Quality Control Division

List of Acronyms (cont.)

WQP	Water Quality Program
YSI	Yellow Springs Instruments

1.0 Background and Study Objectives

This Quality Assurance Project Plan (QAPP) has been prepared by the Denver Department of Environmental Health (DEH) in order to describe water quality monitoring activities performed by DEH in the City and County of Denver (CCoD).

DEH has chosen to develop this QAPP in accordance with United States Environmental Protection Agency (EPA) policy for collection of environmental data by or on behalf of the EPA. The QAPP is a planning document that provides a "blueprint" for obtaining the type and quantity of data needed to support environmental decision-making. The QAPP integrates all technical and quality aspects of a project and documents all quality assurance (QA), quality control (QC) and technical activities and procedures associated with planning, implementing and assessing environmental data collection operations.

This QAPP has been prepared in accordance with the following EPA QA guidance documents:

- *EPA Requirements for Quality Management Plans* (QA/R-2) (EPA, 2001a)
- *EPA Requirements for Quality Assurance Project Plans* (EPA, 2001b)
- *EPA Guidance for Quality Assurance Project Plans* (EPA, 2002a) and
- *Elements of a State Water Monitoring and Assessment Program* (EPA, 2003)

In accordance with these documents, there are four basic groups of elements that must be included in a QAPP. These four groups and associated elements are:

- Group A – Project Management. The elements in this group include all aspects of project management, project objectives and project history.
- Group B – Data Generation and Acquisition. The elements in this group include descriptions of the design and implementation of all measurement systems that will be used during the project.
- Group C – Assessment/Oversight. The elements in this group encompass the procedures used to ensure proper implementation of the QAPP.
- Group D – Data Validation and Usability. The elements in this group cover the QA activities that occur after the data collection phase of the project is completed.

Sections of this QAPP cover each group and the associated elements.

1.1 Problem Identification / Background / Objectives

DEH's Environmental Quality Division (EQD) has been collecting surface water and sediment samples from the streams and lakes in CCoD for over forty years. The sampling program was initially intended to identify and remove illicit connections to the storm sewer system within the CCoD; however, the objectives of the sampling program have evolved over the years to include:

- Assess recreational areas for potential health impacts to users and to post advisories when those waters exceed standards;
- Measure progress towards the City's goals of having all surface waters in Denver be fishable and swimmable;
- Provide recommendations for management of the City's surface waters and address problems before, during, or after they arise;
- Proactively identify and address water quality problems;
- Assess the effectiveness of water quality best management practices (BMPs) at improving water quality;

- Respond to citizen inquires and requests from City and State agencies to support ongoing efforts and initiatives, and;
- Advocate for City positions on development of water quality related regulations and policy.

1.2 Project Organization

The responsibilities for project management, quality assurance, field activities and laboratory protocols are described in the following subsections. An organization chart that identifies the lines of communication among the participants is presented as Figure 1-1 and the responsibilities of project personnel are summarized in Table 1-1.

Management Responsibilities

The Program Manager is responsible for ensuring the overall quality and for completion of tasks associated with the EQD Water Quality Program.

The Project Managers for the EQD Water Quality Program are responsible for developing and maintaining a water quality monitoring program specifically focused on water quality issues of concern. Project Managers are also responsible for scheduling and staffing sampling events, for managing budgets and contracts, for purchasing necessary equipment and supplies for sampling, for ensuring new project personnel are trained in sampling techniques and the use of sampling equipment, for reviewing data to ensure that data quality is sufficient to meet the data quality objectives of the program, for the preparation of all required reports, and for fulfilling any requests for data or information from customers of the Water Quality Program. The Project Manager also ensures resolution of quality issues with the laboratories.

Field Responsibilities

Field Sampling Teams will conduct all field sampling and obtain field measurements for the EQD Water Quality Program. The specific procedures for field sample collection are included in Appendix A. The Field Teams will be responsible for documenting any non-conformances and subsequent corrective actions. The field sampling teams are also responsible for surveying and photographing sample locations as required and updating and maintaining the water quality program GIS databases.

Data Entry Responsibilities

The Data Entry Clerk is responsible for manually entering data into the water quality database as required ensuring that hardcopies of data are filed in the water quality data files.

The GIS Technician is responsible for preparing maps used in reports and presentations, and preparing spatial analysis of data as requested by the Project Managers. The GIS Technician is also responsible for updating and maintaining the water quality program GIS databases as needed.

Laboratory Responsibilities

The majority of the chemical analyses of samples collected during the monitoring program will be performed by contract laboratories. Each laboratory will perform the analytical

procedures at the expected level of quality as detailed in Section 3.0 of this QAPP. The responsibilities of laboratory personnel are summarized in Table 1-1.

Analytical laboratory staffs must demonstrate competence with the training procedures required by each laboratory. Each laboratory complies with the EPA's requirement that the laboratory have a documented quality system.

Project Organization

Figure 1-1 presents the organizational chart for the EQD Water Sampling Program.

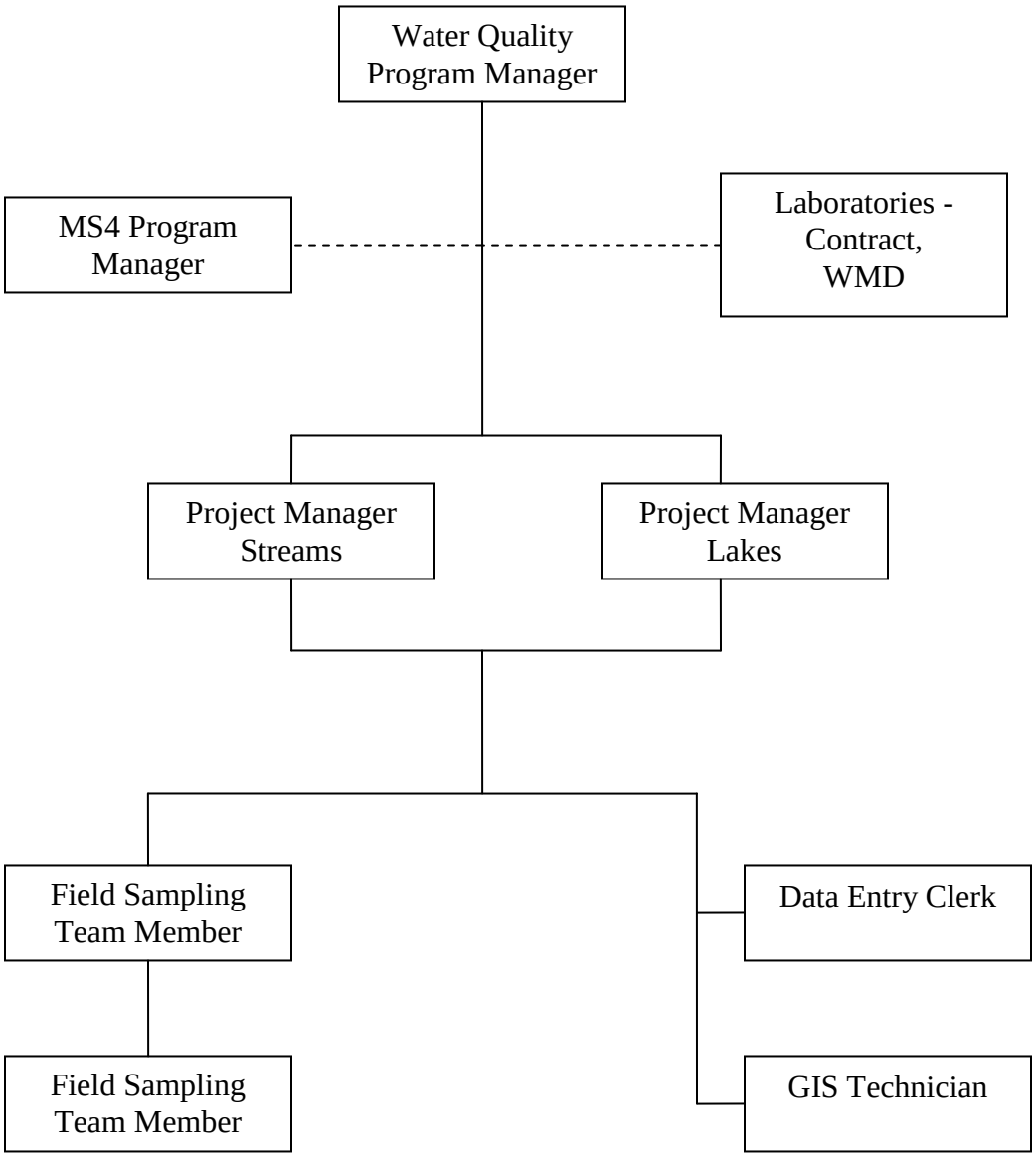


Figure 1-1 EQD Water Quality Program Organizational Chart

Table 1-1 Water Quality Program Responsibilities

Title	Responsibilities
Water Quality Program Manager Liz Babcock (720) 865-5385	• Ensures overall quality of program • Ensures completion of tasks associated with program • Approves expenditures and payment of invoices
MS4 Program Manager Saeed Farahmandi (303) 446-3607	• Ensures overall compliance with terms and conditions of the city's storm water discharge permit
Project Manager Al Polonsky Lakes (720) 865-5480 Jon Novick Streams (720) 865-5468	• Develops and maintains monitoring programs • Schedules and staffs sampling events • Manages budgets and contracts • Coordinates efforts with laboratories • Purchases sampling equipment and supplies • Ensures project personnel are properly trained • Reviews and analyzes data • Ensures data quality is sufficient to meet program data quality objectives • Uploads data into the water quality database • Prepares required reports • Fulfills data and information requests • Point of contact with other stakeholders
Field Sampling Team Member (720) 865-5455	• Conducts field sampling • Obtains field measurements • Surveys and photographs sampling locations as required • Documents non-conformances and corrective actions • Calibrates and maintains sampling equipment • Notifies Project Manager when equipment and supplies are needed
Analytical Services Coordinator Michelle Johnston - TestAmerica (303) 736-0110 Bill Berg – WMD (303) 446-3828	• Ensures requested chemical analyses of samples are performed • Reports results of chemical analyses to Project Managers
Data Entry Clerk Lyda Cimperman (720) 865-5456	• Manually enters data as required • Files hardcopies of water quality data •
GIS Technician Brenda Johnson (720) 865-5471	• Updates and maintains program GIS databases • Creates maps and performs spatial analysis of data for reports as required

Note: Contact information current as of the QAPP revision date.

2.0 Monitoring Objectives

EQD has been collecting surface water and sediment samples from the streams and lakes in CCoD for over forty years. The sampling program was initially intended to identify and remove illicit connections to the storm sewer system within CCoD; however, the purpose of the sampling program has evolved over the years to include:

- Assess recreational areas for potential health impacts to users and to post advisories when those waters exceed standards;
- Measure progress towards reaching the City's goals of having all surface waters in Denver be fishable and swimmable;
- Provide recommendations for management of the City's surface waters and address problems before, during, or after they arise;
- Proactively identify and address water quality problems;
- Assess the effectiveness of water quality BMPs at improving water quality;
- Respond to citizen inquires and requests from City and State agencies to support ongoing efforts and initiatives, and;
- Advocate for City positions on development of water quality related regulations and policy.

The document, *Elements of a State Water Monitoring and Assessment Program* (EPA, 2003) includes five questions that a monitoring program should answer in order to meet the objectives of the Clean Water Act:

1. What is the overall quality of waters in the State?
2. To what extent is water quality changing over time?
3. What are the problem areas and areas needing protection?
4. What level of protection is needed?
5. How effective are clean water projects and programs?

EQD's water quality monitoring program is specifically intended to address four of these five questions (1, 2, 3 and 5) and data from the program is used to support the decision-making process required as part of the other question (4).

2.1 Project Descriptions

In order to meet the goals of the Water Quality Program, EQD subdivides sampling efforts into smaller projects. The goal of each project is described in the following sections.

2.1.1 Trend

EQD's trend monitoring effort is focused on assessment of long-term trends in instream water quality and on assessing the effects of urbanization on the watershed. Sampling efforts associated with trend monitoring are intended to provide data to:

- Measure progress towards reaching the City's goals of having all surface waters in Denver be fishable and swimmable;
- Proactively identify and address water quality problems;
- Assess the effectiveness of water quality BMPs at improving water quality
- Determine the impacts of the upper reaches of the watershed on the receiving water bodies;
- Respond to citizen inquires and requests from City and State agencies to support ongoing efforts and initiatives, and.

The data from trend monitoring are also used to substantiate CCoD positions on policy issues.

2.1.2 Lakes

EQD conducts an annual lake sampling program that strives to ensure the well being of the lake environment and the citizens utilizing the lakes within CCoD. The annual sampling effort typically entails mid-summer visits to fifteen or sixteen lakes in CCoD, with additional sampling as needed. The program focuses on water and sediment quality with an emphasis on parameters that:

- Define water quality conditions within the lake;
- Have standards established by CDPHE, and;
- Are potential hazards identified through site assessment that could influence planning and protocols for site cleanup, renovations, or other CCoD activities.

The purpose of the lake sampling effort is to:

- Identify exceedances of water quality standards;
- Collect data to allow the City to provide meaningful input into the State's 303(d) listing process and into the development of TMDLs;
- Assess the overall health of lake ecosystems;
- Assess long-term trends in water quality, and;
- Provide management recommendations to the City's Parks and Recreation Department.

2.1.3 Monitoring of High Use Areas

From mid-May through mid-October, EQD monitors bacteria levels in streams and lakes where recreational uses have been observed.

Sampling of high use areas is conducted in order to:

- Determine the potential risk to users;
- Identify exceedances of health-based swim beach standards, and;
- Provide information to users so they can be educated on likely bacteria levels and know more about the potential risk of recreating in Denver's urban waters.

2.1.4 Other Sampling Initiatives

In addition to routine monitoring activities and special projects, EQD monitors other locations on an as needed basis or to target specific problem areas. Examples of such projects include demonstrating the effectiveness of water quality BMPs, evaluating the impacts of construction or remediation activities, road construction projects, and one time spills or discharges on water quality, and responses to citizen complaints. The purpose of these monitoring efforts varies from project to project but generally includes the following:

- Assessing the effectiveness of actions taken by the City to improve water quality;
- Environmental and public health oversight;
- Enforcement of local, state, and federal water quality ordinances and regulations as is appropriate, and;
- Developing a better understanding of how stream dynamics affect instream *E. coli* levels.

2.2 Data Quality Objectives

Data quality objectives (DQOs) are statements that define the type, quality, quantity, purpose, and use of the data to be collected. The design of a study is closely tied to the DQOs, which serve as the basis for decisions effecting key design features such as the number and location of samples to be collected and the chemical analyses to be performed. EPA has published a number of guidance documents on the DQO process (EPA, 1994a, EPA, 2000a, and EPA, 2002c). In brief, the DQO process follows a seven step procedure, as follows:

1. State the problem that the study is designed to address
2. Identify the decisions to be made with the data obtained
3. Identify the types of data inputs needed to make the decision
4. Define the boundaries (spatial and temporal) of the study
5. Define the decision rule that will be used to make decisions
6. Define the acceptable limits on decision errors
7. Optimize the design for obtaining data in an iterative fashion using information and DQOs identified in Steps 1 through 6

Following these seven steps helps ensure that the project plan is carefully thought out and that the data collected will provide sufficient information to support the key decisions that must be made.

This QAPP has been developed in accordance with EPA guidance. The following sections summarize the application of the DQO process to the design of the sampling plan for each project.

2.2.1 Data Quality Objectives for Trend Sampling

Figure 2-1 shows the locations of all of the streams in CCoD. The South Platte River, which is the largest feature on the map, flows from south to north and has several tributaries that drain into it within or near the County boundary. South Platte River tributaries include (from south to north): Bear Creek; West Harvard Gulch; Harvard Gulch; Sanderson Gulch; Weir Gulch; Lakewood Dry Gulch; Cherry Creek, and; Sand Creek. Harvard Gulch, Cherry Creek, and Sand Creek drain areas east of the South Platte River and the other tributaries drain the areas to the west. Other tributaries within Denver include Goldsmith Gulch which is a tributary to Cherry Creek and Westerly Creek which is a tributary to Sand Creek. Both Goldsmith Gulch and Westerly Creek drain areas to the south of the receiving creeks.

Step 1. State the Problem
The goal of trend sampling is to provide data to answer several basic water quality-related questions. The questions are:

- What are overall water quality conditions in Denver's streams?
- What progress is being made towards achieving the City's goals of attaining fishable / swimmable waters in Denver (is water quality in Denver's streams improving through time)?
- Are actions taken by the City to improve water quality effective?
- Are there illicit discharges or problem areas that affect water quality?
- Are there any exceedances of water quality standards that could lead to enforcement actions?
- How do the upper reaches of the watershed affect the receiving waters?

EQD's trend monitoring effort represents a long term commitment to answer these questions. Data from trend monitoring efforts is also used to advocate for City positions on development of water quality related regulations and policy

Step 2. Identify the Decision

Trend sampling is conducted to determine overall water quality conditions in Denver's streams. The goals of the sampling effort are stated above. Ultimately, data from trend sampling efforts is used to identify exceedances of instream water quality standards and to determine whether or not mitigation activities or additional investigation are needed to protect human health and the environment (as determined by the State of Colorado instream water quality standards). Data are also used to determine how effective mitigation activities are at improving water quality. The decisions to be made are:

1. Are there any areas where instream standards are exceeded and if so are additional investigation or mitigation efforts necessary?
2. Do long term water quality trends suggest the City is achieving or likely to achieve its internal goals?
3. Do long term water quality trends suggest that actions taken by the City to improve water quality are effective?
4. Do long term water quality trends suggest future exceedances of water quality standards are likely?
5. Does water quality from the upper reaches of the watershed impact receiving waters?

Step 3. Identify Inputs to the Decision

The main input to the decision is the characterization of the concentrations of various pollutants in water. Other inputs into the decision include instream flows, precipitation, and State of Colorado water quality standards. Independent events or incidents, such as faulty or damaged storm and sanitary sewer lines, illegal or illicit discharges, events or incidents that could introduce measurable contamination to the waters (such as firefighting efforts or automobile accidents), can also impact results.

Step 4. Define the Study Boundaries

Spatial Bounds

The spatial bounds of sampling are the corporate boundaries of CCoD. Upstream samples may be collected outside of the boundaries of CCoD if necessary to characterize background or the impact of a specific source on water quality in a stream in Denver.

Temporal Bounds

Trend sampling represents a long term commitment to evaluate water quality conditions in Denver and as a result, the effort is anticipated to be continued on a routine basis for the foreseeable future.

Step 5. Develop a Decision Rule

The decisions to be made above are essentially variations of three questions. Each question, along with the corresponding decision rule, is discussed below.

Are there exceedances of water quality standards?

The rule for decisions related to exceedances of instream water quality is a comparison of sampling results to State of Colorado water quality standards. The comparison will be performed using techniques described in the most current version of the WQCD's document describing the State of Colorado's 303(d) Listing Methodology (WQCC, 2011). An exceedance of a water quality standard occurs when analysis of the data following the methods described in the listing methodology indicates levels of a pollutant in a stream

exceeds the instream standards. The decision to conduct additional investigation or mitigation will be based on the severity of the problem, the potential for a TMDL to be developed and implemented into a City discharge permit, the likelihood that the source can be controlled by the City, and the potential cost of compliance with the water quality standard.

What kind of trends can be observed in analytical results from water quality sampling?

Trend analyses will be conducted using statistical and graphical techniques to determine if sampling results indicate any temporal or spatial water quality trends. The determination if actions are necessary will be based on what, if any trends are indicated.

What impacts do discharges have on the receiving waters?

The impact a discharge from a tributary, problem area, or illicit discharge has on a stream will be determined using statistical techniques providing sufficient data is available to conduct the appropriate analyses. Results from the source and the receiving water will be tested using a means test to determine if an impact on the receiving water is apparent. Additional investigation may be conducted if the means test is inconclusive. The decision to implement mitigation activities or to take enforcement actions will be based on the severity of the problem, an evaluation of the costs and benefits of addressing the problem, and the likelihood that the source can be controlled by the City.

Step 6. Specify Limits on Decision Errors

Sources of errors affecting the decision rule include analytical errors, transcription errors (during input of data into the database), and outliers. EQD attempts to eliminate transcription errors by cross checking data entered into the database against hard copies of the data before conducting data analysis. Both EQD and the WQCD try to address the effects of analytical errors and outliers by evaluating the data with statistical techniques intended to eliminate these sources of error. Even though all of the data is rigorously reviewed prior to use, there are still two types of decision errors that are possible:

1. False Positive Error. For this study, false positive errors could result in the following conclusions:
    a. Trend analysis indicates deterioration in water quality conditions or no progress towards achieving the City's internal water quality goals when water quality conditions are actually stable or improving;
    b. Trend analysis indicates illicit discharges or problem areas along the streams prompting additional investigation and / or mitigation efforts when there are no illicit discharges or problem areas;
    c. Trend analysis indicates that actions taken by the City to improve water quality are not effective when they are;
    d. Evaluation of data indicates exceedances of instream standards prompting additional investigation and / or mitigation efforts when water quality conditions do not exceed standards, and;
    e. Analytical results indicate that water quality in the receiving water is being adversely impacted by discharges from a tributary when it is not.
2. False Negative Error. For this study, false negative errors could result in the following conclusions:
    a. Trend analysis indicates water quality conditions are improving or progress is being made towards achieving Greenprint Denver's goals when water quality conditions are actually getting worse;
    b. Trend analysis indicates there are no illicit discharges or problem areas along the streams when there are;

c. Trend analysis indicates that actions taken by the City to improve water quality are effective when they are not;
d. Evaluation of data indicates no exceedances of instream standards when there are, and;
e. Analytical results indicate that water quality in the receiving water is not being adversely impacted by discharges from a tributary when it is.

For this project, the false positive error rate is set at 20% so that there should be no more than a 20% chance that water quality problems similar to those described above exist when that is not the case. The false negative error rate is set at 5%. There should be no more than a 5% chance that the data indicate that there are no water quality problems similar to those described above when there are.

Step 7. Optimize the Design for Obtaining Results

Analytes

All trend samples are analyzed for indicators of urban pollution. A complete list of analytes can be found in Section 3.

Targeted constituents may also be added or removed from the analytical suite depending on the needs of the program and the frequency of detection.

Sampling Locations

Sampling locations are carefully selected for each stream in Denver in order to ensure sampling adequately characterizes geomorphologically different sections of the stream and to ensure that major sources (such as tributaries, wastewater treatment plants, etc.) are bracketed. The following is a brief description of how sampling locations were selected for each stream. Sampling locations are identified and discussed in more detail in Section 3.1.1.

Sampling Frequency

Trend sampling on Cherry Creek and the South Platte River is coordinated with the sampling efforts of other SP CURE members. The coordinated effort allows for SP CURE members to collect comparable surface water quality data for the entire Denver Metro area.

Samples are collected from all of the other streams and tributaries in Denver at a frequency sufficient to assess potential water quality during different flow conditions.

Additional samples may be collected to verify previous sample results or when conditions might indicate potential contamination.

2.2.2 Data Quality Objectives for Lakes Sampling

Step 1. State the Problem

The lakes within CCoD receive a significant amount of recreational use and provide key wildlife habitat within the metro area. EQD assesses the lakes to ensure their condition does not pose a risk to the public or wildlife as a result of poor water quality or other environmental issues.

Step 2. Identify the Decision

Lake monitoring is performed to identify exceedances of water quality standards and to determine whether or not mitigation activities or additional investigation are needed to protect human health and the environment (as determined by the State of Colorado water quality standards). Data are collected and reviewed to identify areas where contamination

exists at a level of potential concern that requires evaluation of risks to humans and / or ecological receptors. The decisions to be made are:

- Have water quality standards been exceeded in any lakes?
- Is additional investigation necessary in areas where water quality standards were exceeded?
- What, if any, additional mitigation and / or monitoring efforts are necessary in areas where water quality standards were exceeded or where human and / or ecological receptors may be at risk?

Step 3. Identify Inputs to the Decision

Data has been collected from sixteen CCoD lakes annually in mid-summer since 1996. . Targeted compounds for lake sampling are listed in Section 3. The data is analyzed and assessed according to applicable CDPHE water quality standards (WQCC, 2012 and WQCC, 2014) and guidance (CDPHE, 1998 and WQCC 2011).

The sediment data is assessed based on EPA (2001c, 2002d, 2004a) for metals and PAHs and the New Jersey Department of Environmental Protection (2003) for some VOCs. The concentration of constituents in each lake relative to benchmarks based on concentrations from all monitored CCoD lakes also serves as guidance to identify unique situations within the water and sediment.

Additional inputs include current and historical information regarding the lakes. Examples of the former include known existing groundwater plumes. Historical information that can play a key role in the decision making process includes past land use practices that may have impacted the lake water and/or sediment quality.

Step 4. Define the Study Boundaries

Spatial Bounds:

Figure 2-2 is a map of Denver lakes that are sampled annually. Two to five sites are sampled at each lake so as to characterize the inlet region, outlet region, and the middle or deepest portion of the lake. Lakes with irregularly shaped perimeters and/or islands may have additional sample locations to adequately characterize the entire lake. The central and/or deepest portion of the lake are typically used for the more intensive sampling (temperature-D.O. profiles, bacteria, chlorophyll-a, and sediment sampling). Maps of each lake with designated sample site locations are included in Section 3.

Temporal Bounds:

The annual sampling effort typically occurs from mid July through mid-August, with additional sampling as needed. Because of high recreational use, Sloans Lake is also sampled weekly from May through September to assess bacteria concentrations.

Step 5. Develop a Decision Rule

EQD evaluates data collected as part of lake sampling to assess current status and long-term trends in water quality. Data are examined for temporal and spatial trends using graphical techniques to identify areas of concern which may require further investigation and / or mitigation.

Data from lake sampling is also provided to the WQCD every two years as part of the 303(d) listing process. The WQCD analyzes data provided by EQD and other sources as described in WQCC (2011) to determine if any of the analytes exceed water quality standards. If the analysis of the data indicates that any constituent exceeds state

standards, the lake will be added to the State's list of impaired waters (the 303(d) list) for further monitoring and evaluation or for development of a TMDL.

Step 6. Specify Limits on Decision Errors
Sources of errors affecting the decision rule include analytical errors, transcription errors (during input of data into the database), and outliers. EQD attempts to eliminate transcription errors by cross checking data entered into the database against hard copies of the data before conducting data analysis. Both EQD and the WQCD try to address the effects of analytical errors and outliers by evaluating the data with statistical techniques intended to eliminate these sources of errors. Even though all of the data is rigorously reviewed prior to use, there are still two types of decision errors that are possible:

1. False Positive Error – analytical results indicate that lake water quality conditions are not in compliance with instream standards when they are, and;
2. False Negative Error – analytical results indicate that lake water quality conditions are in compliance with instream standards when they are not.

For this project, the false positive error rate is set at 20% so that there should be no more than a 20% chance that lake water quality standards are indicated to be exceeded when they are not. The false negative error rate is set at 5%. There should be no more than a 5% chance that analytical data indicates that lake water quality standards are not exceeded when they actually are.

Step 7. Optimize the Design for Obtaining Results
DEH lake sampling protocols are based on those implemented and suggested by the CDPHE, EPA, or other appropriate entities (i.e., Denver Water Board for chlorophyll-a analysis). The Denver lakes are sampled from mid July through mid-August to assess conditions during the growing season and during times of peak recreational use. To minimize seasonal bias, the annual mid-summer sample period is kept to as tight a schedule as possible (less than one month) to allow for comparison of results within all the lakes for the year, as well as accommodating comparisons to results from previous years. While occasional sampling does occur as needed during other times of the year, these results are used to assess seasonal changes and as supportive information for purposes as needed (i.e., sediment characterization for cleanup or renovation assessment).

Upon accumulation of an adequate amount of data (3-5 annual visits), the number of monitoring sites sampled per each lake will be assessed to determine an acceptable minimal number. This determination will be based on variability of the data between the sites within each lake over the years sampled. Each lake will be considered individually. The need for this assessment will be determined prior to each mid-summer sampling round.

2.2.3 Data Quality Objectives for Monitoring of High Use Areas

Step 1. State the Problem
A number of waterbodies in Denver receive heavy recreational use and although none are designated by CCoD as natural swim areas (wading and swimming does occur at several locations, however; boating and water skiing are the allowable recreational uses), EQD is concerned that people interacting with water in the City's streams and lakes may be exposed to health risks.

Step 2. Identify the Decision
The overall decision is whether or not any areas used for recreation are unsafe for human contact.

Step 3. Identify Inputs to the Decision
The main inputs to the decision are characterization of levels of bacteria in water and state swim beach standards (CDPHE, 1998).

Step 4. Define the Study Boundaries

Spatial Bounds
The spatial bounds of sampling are the corporate boundaries of CCoD. Any stream or lake within Denver which is known to have recreational uses is sampled by this project.

Temporal Bounds
Sampling is conducted in accordance with the State of Colorado swim beach standards (CDPHE, 1998). Sampling is conducted during the period of heaviest use (Early May through October) with sampling frequency based on amount of use and results from previous sampling.

Step 5. Develop a Decision Rule
EQD evaluates data collected as part of this project to identify potentially unsafe conditions. Sampling and data analysis is conducted in accordance with the requirements of CDPHE (1998). If sampling indicates that bacteria levels exceed the Colorado swim beach standards, users will be alerted that the water contains unsafe levels of bacteria.

Step 6. Specify Limits on Decision Errors
Sources of errors affecting the decision rule include analytical errors, transcription errors (during input of data into the database), and outliers. EQD attempts to eliminate transcription errors by cross checking data entered into the database against hard copies of the data before conducting data analysis. Both EQD and the WQCD try to address the effects of analytical errors and outliers by evaluating the data with statistical techniques intended to eliminate these sources of errors. Even though data is rigorously reviewed prior to use, there are still two types of decision errors that are possible:

1. False Positive Error – analytical results indicate that swim beach standards are exceeded when they are not, and;
2. False Negative Error – analytical results indicate that swim beach standards are not exceeded when they are.

Since determination that bacteria levels exceed swim beach standards could have both economic and social impacts and since some areas are destinations for users (i.e. they may travel out of their way to get there), the false positive error rate is set at 10% for this project. There should be no more than a 10% chance that analytical results indicate swim beach standards are exceeded when they are not. Because the potential for human exposure to bacterial pathogens is high, the false negative error rate is set at 5%. There should be no more than a 5% chance that analytical data indicates that swim beach standards are not exceeded when they actually are.

Step 7. Optimize the Design for Obtaining Results
As described above, high use areas are sampled regularly during warmer weather to provide regular updates on bacterial levels. Sampling is conducted to ensure adequate time to take appropriate actions prior to weekends or holidays when use is highest. Analytical parameters are dictated by CDPHE (1998), however; sampling locations may be changed if usage patterns or the needs of this project change.

2.2.4 Data Quality Objectives for Other Sampling Efforts

In addition to routine monitoring activities and special projects, EQD monitors other locations on an as needed basis or to target specific problem areas. Examples of such projects include demonstrating the effectiveness of water quality BMPs, evaluating impacts of construction or remediation activities, one-time spills or discharges on water quailty, and in response to citizen complaints. The purpose of these monitoring efforts varies from project to project but generally includes the following:

- Assessing the effectiveness of actions taken by the City to improve water quality;
- Environmental and public health oversight;
- Enforcement of local, state, and federal water quality ordinances and regulations as appropriate, and;
- Developing a better understanding of how stream dynamics affect instream E. coli levels.

If deemed necessary, DQOs will be developed on a case-by-case basis for any other sampling needs that arise.

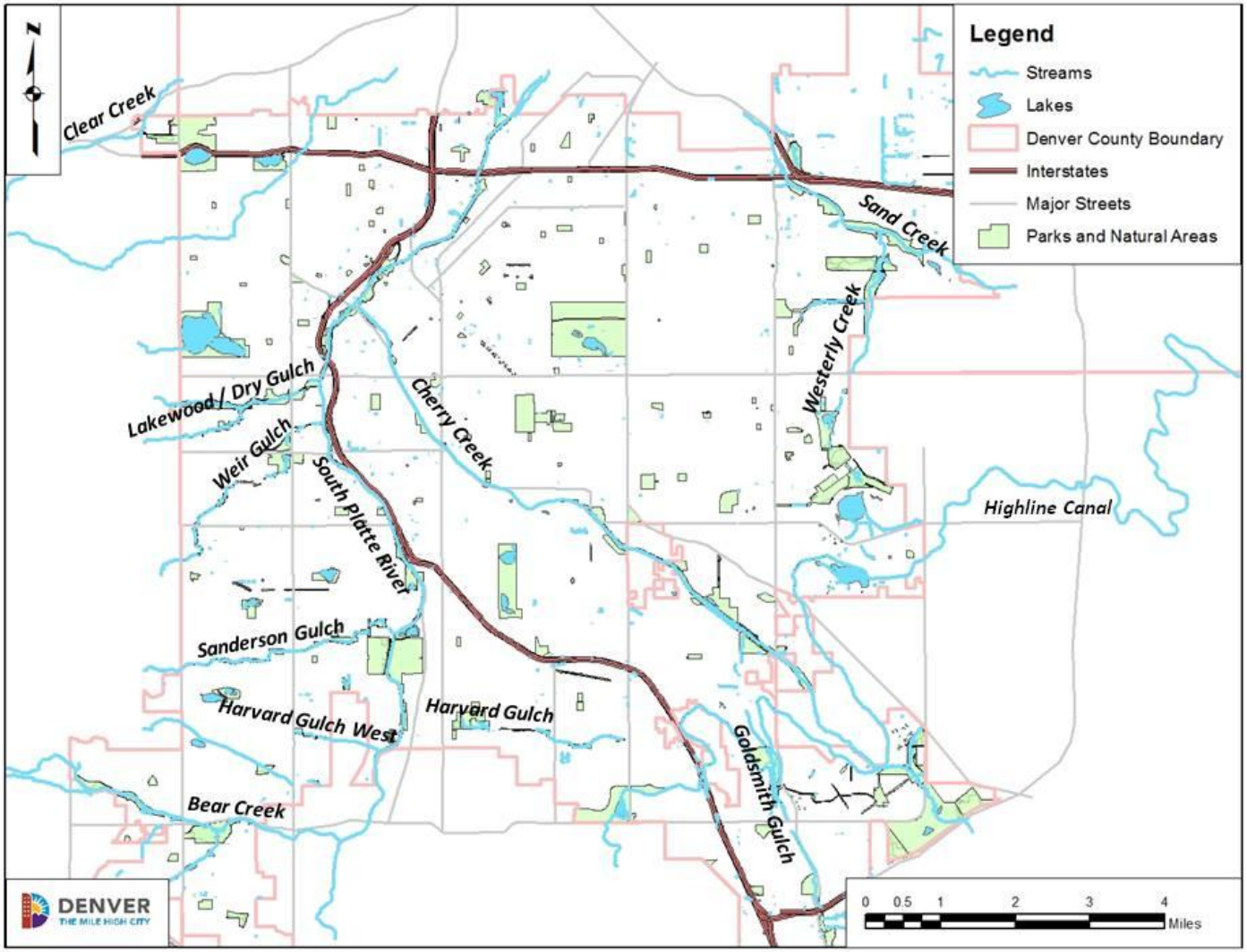


Figure 2-1 Locations of Streams in Denver

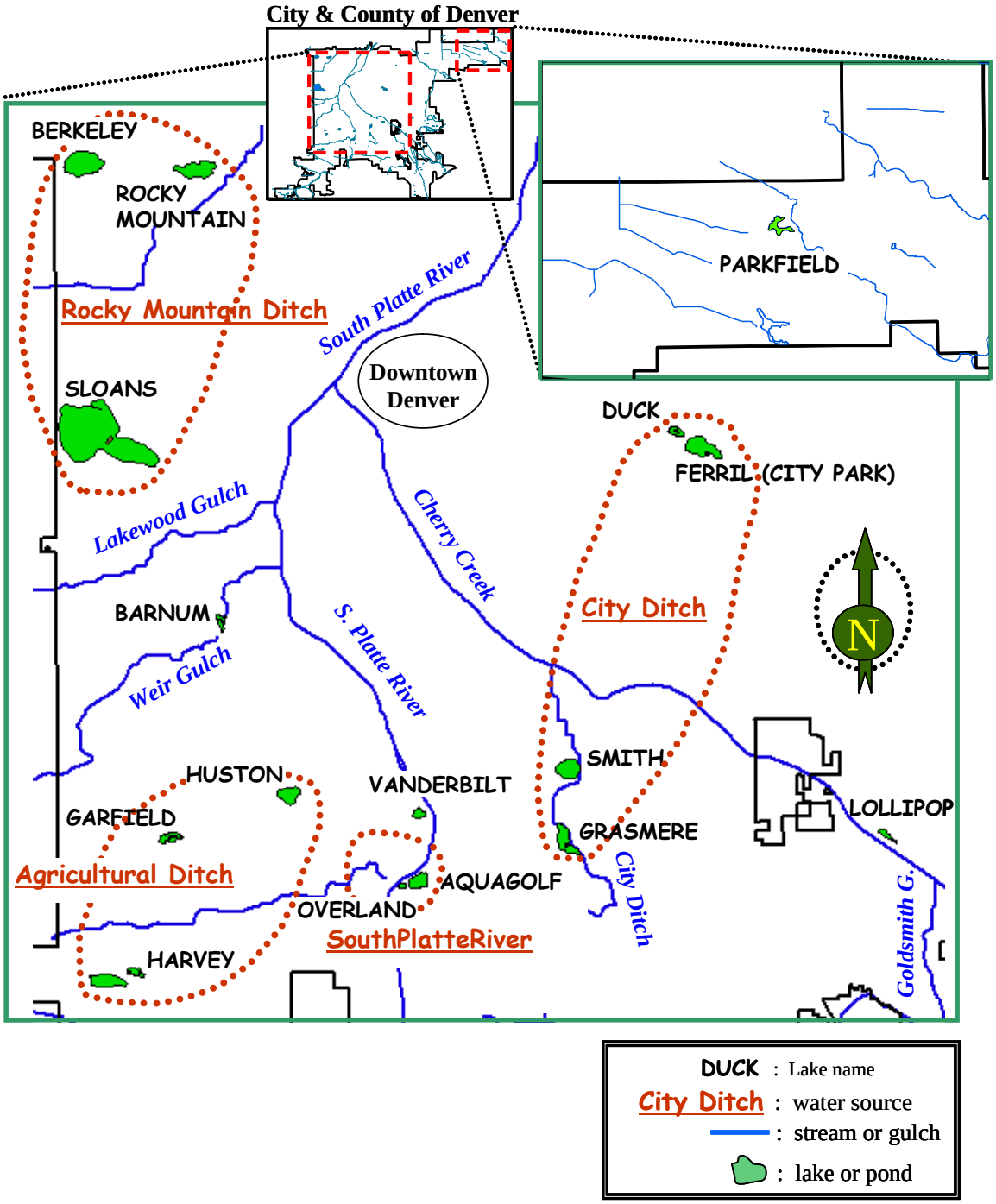


Figure 2-2 Locations of Lakes in Denver

3.0 Data Measurement and Acquisition

This section describes EQD's Water Quality Sampling Program data collection methods, sampling approach, and data management and QA/QC efforts. Specific aspects of this section include:

- Basic monitoring program approach and sample site selection;
- Sampling methodologies including sample handling and chain of custody procedures;
- Analytical methods;
- Field and laboratory QA/QC methodologies;
- Field and laboratory meter calibration and maintenance;
- Data management including database operations and analyses.

3.1 Sampling Process Design

EQD's Water Sampling Program includes a number of projects. Each project is described, along with project goals in Section 2.1. This section describes each project's data collection and monitoring approach. Each project description includes a summary of sample locations, sampling frequency, and analytes. The rationale for selection of sampling locations, analytical parameters, and sample frequency is included in each summary. The rationale includes a summary of how the design of each project will meet the project's goals. Table 3-1 summarizes the analytical parameters for each project.

3.1.1 Sampling Sites

Trend

EQD conducts a coordinated sampling effort with SP CURE that is focused on assessment of water quality trends in the South Platte River and Cherry Creek. Sampling is also conducted on all of the other small streams in Denver to assess water quality trends and the impact of the upper reaches of the watershed on the South Platte River and Cherry Creek. The goal of trend sampling is to measure progress towards reaching the City's goals of having all surface waters in Denver be fishable and swimmable, proactively identify and address water quality problems, assess the effectiveness of water quality BMPs at improving water quality, and determine the impacts of the upper reaches of the watershed on the receiving water bodies. Trend sample locations are shown in Figure 3-1. Samples are analyzed for indicators of urban pollution; nutrients, solids, selected cations, metals, and bacteria (Table 3-1). Many of these analytes have instream water quality standards (WQCC, 2012, WQCC, 2014). Sampling frequency is summarized in Table 3-2.

South Platte River
SP CURE initially selected four sampling locations on the South Platte River in Denver. The locations were selected to document water quality impacts from major sources on the river (Cherry Creek, an outfall called N-433-E, and the National Western Stock Show). Additional sampling locations were added to the South Platte River in 2005 to provide data on water quality in the upstream part of the river in CCoD. In order to facilitate the selection of the additional sampling locations, the South Platte River in Denver was sub-segmented based on stream morphology and potential pollutant inputs. A description of each sub-segment can be found in EQD (2005). The additional sampling locations were selected so that at least one sample is collected from each sub-segment. Figure 3-1 shows the South Platte River trend sampling locations.

South Platte trend sampling is conducted on the first Wednesday of every month in coordination with other members of SP CURE. The coordinated effort allows for SP CURE members to collect comparable surface water quality data for the entire Denver Metro area.

Cherry Creek
SP CURE initially selected one sampling location on Cherry Creek in Denver (at the US Geological Survey (USGS) gauge at Champa St.). The location was selected to document water quality in Cherry Creek immediately upstream from its confluence with the South Platte River. Additional sampling locations were added to Cherry Creek in 2003 to provide a better understanding of upstream water quality conditions. As was done for the South Platte River, Cherry Creek in Denver was sub-segmented based on stream morphology and potential pollutant inputs. A description of each sub-segment can be found in EQD (2005). The additional sampling locations were selected so that at least one sample is collected from each sub-segment. Figure 3-1 shows the Cherry Creek trend sampling locations and the analyses are summarized in Table 3-1.

Cherry Creek trend sampling is conducted on the third Wednesday of every month in coordination with other members of SP CURE. The coordinated effort allows for SP CURE members to collect comparable surface water quality data for the entire Denver Metro area.

Bear Creek
EQD started trend sampling on Bear Creek in 2007. Sampling locations were selected based on stream morphology and potential pollutant inputs. Figure 3-1 shows the Bear Creek sampling locations and Table 3-1 summarizes sample analyses. Bear Creek is sampled quarterly.

Westerly Creek
Sampling of Westerly Creek began in 2001 and was initially intended to assess the effects of development at Stapleton on the watershed. In 2014 and 2015, EQD added a sampling location (WN11) to assess the quality of water discharging from Kelly Road Dam and then eliminated sampling at all except one of the Stapleton sites in an effort to more evenly distribute sampling locations through the watershed. Sampling locations are shown in Figure 3-1 and analyses are summarized in Table 3-1. EQD samples Westerly Creek quarterly.

Other Tributaries
EQD routinely collects instream samples from all tributaries in Denver to assess water quality impacts from the upper reaches of the watershed. There are six tributaries included in this effort; Harvard Gulch (S-242-E), West Harvard Gulch (S-271-W), Sanderson Gulch (S-142-W), Weir Gulch (N-91-W), Lakewood Gulch (N-142-W), and Goldsmith Gulch (CE-671-S). Locations of the tributaries locations are shown in Figure 3-1. Samples are collected quarterly from all of these streams immediately upstream of their confluence with the receiving waters in order to asses potential water quality impacts from the upper reaches of the watershed during different flow conditions. Sample analyses are summarized in Table 3-1.

Lakes

The primary objective of the EQD Lakes Program is to characterize the lake water and sediment quality during the growing season; the time of year in which lake eutrophic status is most readily discernable.

EQD samples approximately sixteen lakes per year (Figure 2-2). Most of the lakes are sampled at the inlet area, the outlet area, and the mid-lake region. Exceptions are made for lakes with unique configurations or sizes such as islands, inlets and / or outlets near each other or near the middle of the lake. The number of sampling locations may be limited to one or two sites if the surface size does not justify the need for three sites to characterize the entire water body. Specific sampling locations for each lake are shown in Figures 3-2 through 3-16. The central and/or deepest portion of the lake are typically used for the more intensive sampling (temperature-DO profiles, bacteria, chlorophyll-a, and sediment sampling).

Monitoring of High Use Areas

EQD routinely monitors bacteria levels at several locations from May through October to assess health risks for users. Sampling locations are shown in Figure 3-17. Confluence Park and Bear Creek are sampled weekly, Sloans Lake is sampled every two weeks, and Westerly Creek, Cherry Creek at Holly, Berkeley Lake and Sloans Lake are sampled once or twice a month. The Confluence is also sampled twice a month throughout the rest of the year. All of these areas receive heavy recreational use, Sloans Lake by water skiers, Berkeley and Rocky Mountain Lakes by boaters, the Confluence area by kayakers and waders, and the Bear Creek swimming hole, Cherry Creek at Holly, and Westerly Creek by waders. EQD has elected to follow a modified version of CDPHE regulations governing "natural swim areas" (CDPHE, 1998) although none of the locations are actually designated as one. The regulations include requirements for sampling locations and frequency at natural swim areas. Specific requirements of the regulation that EQD follows include:

- Samples must be collected from areas of the greatest bather load or activity, and;
- Samples must be collected from within twelve inches of the water's surface.

Sampling locations at all of the sites correspond to the areas with highest recreational use. The analytical suite for sampling in high use areas is summarized in Table 3-2.

Other Sampling Initiatives

In addition to routine monitoring activities and special projects, EQD monitors other locations on an as needed basis. The sampling locations, analytical requirements, and sampling frequency vary depending on the requirements of the monitoring activities. EQD generally prepares sampling plans for any sampling initiative that involves routine sampling. Each sampling plan will include any sampling-related topics not included in this QAPP.

3.2 Sampling Methodologies

All sampling conducted by EQD is performed in accordance with EQD's sampling procedures. Copies of all EQD procedures related to surface water and sediment sampling are included in Appendix A.

3.3 Sample Handling and Chain of Custody Requirements

3.3.1 Field Documentation

Field Logbook
Each sampler will carry a field logbook in which the following information is recorded:

- Sample date
- Sample personnel

- Weather conditions
- Sample location
- Time sample collected
- Field measurements
- Field instrument calibration data for parameters calibrated in the field
- Any additional information

Field forms
Electronic copies of the WMD Laboratory Field / Chain of Custody (COC) Forms are available to all samplers. When possible, it is preferable to complete as much information as possible on the forms before leaving the office. This will prevent transcription errors when the data is entered into the database. Blank extra forms should always be taken in case they are needed. Completion of field forms is discussed in EQD Procedures ST-004 (Using Field Forms) and LK-002 (Field Forms) which are included in Appendix A.

Each field form is completed on site at the time sampling occurs. Field technicians record the site number, date and time the sample was collected, the initials of each person present, precipitation at the time of sampling (or within the 24 hours preceding the sampling), and any other information pertinent to the collection of the sample. Field sampling team members also record all field measurements (pH, temperature, specific conductivity, dissolved oxygen, turbidity, and flow if appropriate) on the field form for each sampling location.

Sample Handling, Chain of Custody, and Sample Shipment
All samples will be handled in accordance with the methods presented in the EQD Procedures LK-001 (Lake Sampling), ST-001 (Surface Water Sampling), ST-002 (Outfall Sampling), and ST-003 (Stream Sediment Sampling), and ST-007 (Procedure for Field Filtration of Water Samples) included in Appendix A.

Contract Laboratory Chain of Custody Forms
A contract laboratory COC form shall accompany every shipment of samples to the contract analytical laboratory. The purpose of the COC is to provide documentation that traces sample possession from the time of collection through analysis and to final disposal. The COC is also used to indicate which analyses are to be performed. Following COC procedures establishes a legally defensible record and prevents potential tampering with or loss of samples. The COC form will be completed in the field as samples are collected and filled out with indelible black ball-point ink. Any corrections will be made by drawing a single line through the error and will include initials of the person making the corrections and the date the corrections were made. Each COC form will include signatures of the appropriate individuals indicated on the form. Every time possession of the samples is transferred they must be released and accepted by signature on the COC form. The sampler should retain a copy of the COC either prior to sealing the sample cooler for transport to the laboratory or upon acceptance of samples if the sampler delivers them to the laboratory. A second copy is also kept by the laboratory after samples are logged in.

Electronic copies of the COC are available to all samplers. When possible, it is preferable to complete as much information as possible on the forms before leaving the office. This will prevent transcription errors when the data is entered into the database. Blank extra forms should always be taken in case they are needed.

Sample Labels
When samples are collected, each container will have a sample label affixed to the outside of the container. The label will include the sample location, date, time and requested

analysis. The sample label should also be signed by the sampler. The information on the sample label must match the COC form exactly. Any discrepancies will be noted by the laboratory and the Project Manager will be notified to ensure correct sample identification.

Sample Shipping
Samples will be transported to the laboratory by a laboratory courier or the sampler will drop them off. Upon arrival at the laboratory, the sample custodian will open the cooler and inspect the contents. The temperature of the contents will be recorded, COC forms will be inspected for completeness and samples will be logged and assigned a unique laboratory ID number. Any discrepancies or abnormalities will be recorded and the Project Manager will be notified. The discrepancies will also be described in the case narrative of the final data package.

3.4 Analytical Methods

To ensure that the DQOs established in this QAPP can be achieved, the analytical criteria that are to be used for data generation by laboratory analysis must be clearly identified. Analytical methods for sample analyses are selected on the basis of the contaminants of concern and the required detection limits. For the water quality sampling program, detection limits are based on instream water quality standards, where standards are available, or on the DQOs for the project if standards are not available. Instream water quality standards and required detection limits are presented in Table 3-3. Table 3-4 identifies analytical methods, method numbers, reference guidance, sample container and sample volume requirements, sample preservatives, and sample holding times for samples collected during sampling activities.

3.5 Quality Assurance / Quality Control

QA is an integrated system of quality planning, assessment, and improvement activities intended to provide a project with a measure of assurance that the established standards of quality are met. EQD's QA Program is designed to measure the precision, accuracy, representativeness, comparability, and completeness of data generated by water quality sampling efforts.

Precision: Precision is defined as the agreement between a set of replicate measurements without assuming or knowing the true value. Agreement is expressed as either the relative percent difference for replicate measurements or the range and standard deviation for larger numbers of replicates. Data on precision are obtained by analyzing replicate samples.

Accuracy: Accuracy is a measure of the closeness of sample analysis results to the true value. The accuracy of an analytical method is generally assessed by inserting a series of double blind performance evaluation samples in to the laboratory sample stream where the true concentration of the analyte in each double blind sample is known.

Representativeness: Representativeness is the degree to which data accurately and precisely represent characteristics of a population parameter, variations at a sampling point, or an environmental condition. For this QAPP, Representativeness is ensured by the selection of sampling locations in accordance with the sampling design requirements.

Comparability: Data are comparable if collection techniques, measurement procedures, methods, and reporting units are equivalent for the samples within a sample set. These criteria allow comparison of data from different sources. Comparable data will be obtained

by specifying standard units for physical measurements and standard procedures for sample collection processing and analysis. These requirements are specified in SOPs included in Appendix A for sampling procedures and in Table 3-4.

Completeness: Data are considered complete when a prescribed percentage of the total intended measurements and samples are obtained. Analytical completeness is defined as the percentage of valid analytical results requested. For this sampling program, collection of samples at a minimum of 80% of the planned sampling locations must be obtained to achieve a satisfactory level of data completeness.

QC checks, including both field and laboratory, are specific operational techniques and activities used to fulfill the QA requirements.

3.5.1 Field Quality Control

Field QC samples are submitted as separate samples to the laboratory and reported accordingly on the data reports. Specific requirements are outlined below. The only field QC samples routinely used on this program are field replicates.

Field Replicates
Field replicates are co-located samples collected from one sample location in order to measure analytical accuracy. Replicate samples are collected at a frequency of 5% (one replicate sample per twenty samples). Replicate samples are collected, sealed, handled, stored, shipped, and analyzed in the same manner as the primary sample. Detailed procedures for collecting replicates are described in sampling procedure ST 006 (Procedure for Collecting QC Samples) which can be found in Appendix A. Precision of replicate results is calculated by the relative percent difference (RPD) as defined by 100 times the difference (range) of each replicate set, divided by the average value (mean) of the set. For replicate results, R1 and R2, the RPD is calculated from the following equation:

Equation 1 Field Relative Percent Difference

$$RPD = \frac{((R1 - R2) * 100)}{\left(\frac{(R1 + R2)}{2}\right)}$$

Best professional judgment is used to determine the acceptability of field replicate analyses.

Split Samples
Split samples are co-located samples that are collected and sent to a second laboratory for analysis. The results will be compared to ensure that Laboratory results are accurate. EQD collects split samples if there is concern about the accuracy of the Laboratory's results.

Trip Blanks
Trip blanks are used to assess contamination introduced into the sample by VOCs during transport of samples. Trip blanks are only collected when samples are to be analyzed for VOCs. Trip blanks are prepared prior to sampling and consist of deionized or distilled water that is taken to the field in sealed sampling containers. The trip blanks remain in the sealed container with the VOC samples until they are analyzed along with the samples at the contract laboratory.

Field Blanks
Field blanks consist of deionized or distilled water that is taken to the field, transferred to the appropriate container, preserved, and otherwise treated as a sample during the course

of a sampling event. The analysis of field blanks should yield values that are less than the practical quantitation limits of the analytical instruments. EQD currently collects field blanks one or two times a year.

Equipment Rinsate Blanks
Equipment rinsate blanks provide evidence that sampling equipment is being adequately cleaned and cross contamination is not occurring. After sampling equipment has been decontaminated, water from the final equipment rinse is collected and sent for analysis. Equipment rinsate blanks are collected at 5% (one equipment rinsate blank for every twenty samples) of the sampling locations, if sampling equipment is reused. If sampling equipment is not reused as part of the sampling effort, equipment blanks are not necessary.

Double Blind Samples
Double blind samples are used to check the accuracy of the analytical methods specified and to assess the performance of laboratories performing analyses for the water quality program. Double blind samples are sent to the laboratory at the discretion of the sampling team lead. Double blind samples are prepared and certified by a vendor in the Laboratory's sample containers.

3.5.2 Laboratory Quality Control

Analyses of samples collected by CCoD are performed by laboratories that have established laboratory QA plans in compliance with the EPA's QA guidance for sampling and chemical analysis. The Water Quality Program currently uses the City's Wastewater Management Laboratory and a contract laboratory to perform analyses. Contact information for each laboratory is maintained by the Project Managers. Each laboratory operates under its own Quality Assurance Manual. Copies of the WMD QA Summary are included in Appendix C. The contract laboratory Quality Assurance Manual is available upon request from the contract laboratory. Detailed laboratory QC requirements are contained within the laboratory Quality Assurance Manual and are also specified in the EPA approved analytical methods. All laboratories used for the Water Quality Program will also operate in accordance with this QAPP. Minimum requirements that all participants abide by are stated below.

Laboratory Custody Procedures
The analytical laboratory assumes responsibility for the integrity and security of the samples upon receipt of samples and completion of the chain of custody transfer.

The Analytical Services Coordinator for the laboratory receives the samples, assigns the laboratory number for each sample container on the chain of custody record, and logs the samples into the sample / data control system along with all necessary information related to sample identity.

The Analytical Services Coordinator checks each sample to ensure that the samples are properly coordinated with field book information, chain of custody records, and all other pertinent information. The samples are then put into a secured storage area.

Authorized laboratory personnel may then obtain the samples from the secured storage area. The analysts are held responsible for returning all samples to the secured storage area upon completion of analyses.

When samples are transferred from the laboratory to any other destination, the appropriate chain of custody protocol will be followed. Contract laboratories will retain the samples for

thirty days after submittal of the final analytical report. At the end of thirty days, the laboratories will properly dispose of the samples.

Calibration Procedures and Frequency
All laboratory instrumentation must be calibrated prior to use. Laboratory instruments must be calibrated using calibration blanks and standards following EPA (1983), EPA (2000a), EPA (2005), or the American Public Health Association (APHA, 2005) protocols as applicable. Divergence from acceptable benchmark criteria, as defined by method-specific protocol and instrument type, requires correction before analyses can be performed. Calibration, blank and instrument performance standard check results must be recorded in the instrument log book, which will also contain evaluation parameters, benchmark criteria and maintenance records. Standard Reference Materials from the National Institute of Standards and Technology (NIST), the EPA or other certifiable sources should be obtained and analyzed to assess and assure the accuracy of the measurement parameter.

Laboratory Duplicates
Laboratory duplicates are used to assess precision. A laboratory duplicate is prepared by splitting aliquots of a single sample (or a matrix spike or a laboratory control standard) in the laboratory. Both samples are carried through the entire preparation and analytical process. Laboratory duplicates are performed on 10% of samples analyzed. Precision is calculated by the RPD of duplicate results as defined by 100 times the difference (range) of each duplicate set, divided by the average value (mean) of the set. For duplicate results, D1 and D2, the RPD is calculated from the following equation:

Equation 2 Laboratory Relative Percent Difference

$$RPD = \frac{((R1 - R2) * 100)}{\left(\frac{(R1 + R2)}{2}\right)}$$

Laboratory Control Sample
A laboratory control sample (LCS) is analyte-free water spiked with the analyte of interest prepared from standardized reference material. The LCS is generally spiked at a level less than or equal to the mid-point of the calibration curve for each analyte. The LCS is carried through the complete preparation and analytical process. The LCS is used to document the accuracy of the method due to the analytical process. LCS's are generally run at a rate of one per batch. Acceptability criteria are laboratory specific and usually based on results of past laboratory data. The analysis of LCS's is a measure of accuracy and is calculated by %R and defined as 100 times the observed concentration, divided by the true concentration of the spike. Acceptance criteria are based on laboratory control charts, but not greater than the prescribed criteria. The formula to calculate %R uses SR, the sample result, and SA is the spike added:

Equation 3 Laboratory Control Sample Percent Recovery

$$\%R = \frac{(SR * 100)}{SA}$$

Matrix Spikes
A matrix spike (MS) is an aliquot of sample spiked with a known concentration of the analyte of interest. Percent recovery of the known concentration of added analyte is used to assess accuracy of the analytical process. The spiking occurs prior to sample preparation and analysis. The MS is spiked at a level less than or equal to the midpoint of the calibration or analysis range for each analyte. The MS is used to document the accuracy of

a method due to sample matrix and not to control the analytical process. The analysis of matrix spikes is a measure of accuracy and is determined by %R. %R is defined as 100 times the observed concentration, minus the sample concentration, divided by the true concentration of the spike. The formula used to calculate %R, where SSR is the observed spiked sample concentration, SR is the sample concentration, and SA is the spike added is:

Equation 4 Matrix Spike Percent Recovery

$$\%R = \left(\frac{(SSR - SR)}{SA}\right) * 100$$

Method Blanks
A method blank is an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination in the preparatory and analytical processes. The analysis of method blanks will yield values less than the Minimum Analytical Level. For very high-level analyses blank value will be less than 5% of the lowest value of the batch.

Additional Method Specific QC Requirements
Additional QC samples are run (e.g., surrogates, internal standards, continuing calibration samples, interference check samples) as specified in the analytical methods. The requirements for these samples, their acceptance criteria, and corrective action are method-specific and are therefore not listed in this plan.

Other Requirements
If the Project Manager, in conjunction with the Analytical Services Coordinator find the analytical data to be unreliable or incomplete, the laboratory is responsible for correcting the errors. If the laboratory cannot provide data of adequate accuracy and precision, the samples may need to be recollected.

3.6 Instrument and Equipment Inspection, Maintenance, and Calibration

Water quality meters used for routine field analysis are listed in Table 3-5. This section documents calibration, inspection, and maintenance protocols for all listed meters. It will also list other sampling equipment and appropriate information to assist with long term maintenance and to expedite repairs as needed.

There are several pieces of non-meter equipment utilized by the lake sampling program on a routine basis (Table 3-6). Relevant information for maintenance of this equipment will also be provided in this section.

3.6.1 Instrument Calibration, Inspection, and Routine Maintenance

Meters-Calibration
All field meters are to be calibrated by Field Sampling Team Members in the EQD laboratory on the day they will be used, prior to sampling. Calibration protocols are provided in Appendix A and also in the Meter Calibration and Maintenance Log (MCM Log) which is stored in the EQD laboratory with the meters. More detailed calibration information is provided in the factory provided meter-specific manuals which are stored in the laboratory. All calibration activities are documented in the MCM Log on the Meter Calibration - Quality Control forms (Appendix B). Problems with calibration are to be reported to the Project

Manager. Calibration timing, frequency, and responsible personnel are summarized in Table 3-7.

Meters-Inspection
Field meters should be inspected upon each calibration and routine maintenance by Field Sampling Team Members. The inspection entails ensuring the probes are intact and that the DO probes have no bubbles within the fluid. Inspection frequency and responsible personnel are summarized in Table 3-7.

Meters-Routine Maintenance
Primary routine maintenance activities for field meters include renewal of calibration standards (pH, conductivity, and turbidity) and replacement of DO probe solutions and membranes. The frequency and personnel responsible for maintenance of the EQD meters is summarized in Table 3-7. Calibration standards are also included in Table 3-7. Conductivity and pH standards should be kept covered and in a cabinet when not being used. Turbidity standards should be refrigerated. In the event that a standard is left uncovered for a significant amount of time, it should be replaced immediately. Calibration standards and DO probe caps, membranes, and solution are stored in the cabinet above the sink near the meters in the EQD Laboratory.

Non-meter Inspection and Routine Maintenance
Inspection of non-meter field equipment should be done during preparation for a sample season or event, upon each sample event, when washing the equipment, and upon completion of a sampling season or event. Routine maintenance can include calibration of water depth markings (i.e., secchi disc, manual depth finder), patching holes in waders, and replacing soles on wader boots. Non-meter inspection and maintenance details are provided in Table 3-8.

3.6.2 Instrument Maintenance – Non-Routine

When accidents or equipment failures occur, it is essential that the appropriate personnel are informed. If a meter or piece of equipment can be repaired in-house, it should be done immediately to ensure that all EQD resources are available for use. Immediate attention will also allow for a determination on whether it is necessary to seek additional assistance for the equipment repair. Relevant phone numbers and addresses for meter and non-meter equipment are listed in Tables 3-7 and 3-8. All maintenance actions should be recorded in the meter-specific manual and in the MCM Log. Spare parts are labeled and stored in the EQD Laboratory.

3.7 Inspection / Acceptance Requirements for Supplies

This Section identifies critical project supplies and personnel who are responsible for making sure that they are available. Procurement of critical equipment and supplies and verification that the equipment and supplies received met the required specifications is a critical step to maintain the quality of samples collected under this program. Once procured items are received, receiving personnel will ensure that the items received are in conformance with the specifications of the order. Any items determined to not be in conformance will be returned to the vendor for replacement or repair.

EQD has identified three types of supplies that are critical to the water quality monitoring program; calibration solutions, double blind samples, and sample containers.

Calibration solutions are used to ensure that readings taken using water quality meters are accurate. EQD currently obtains calibration solutions from a number of vendors. Calibration solutions are purchased on an as needed basis. Field Team Members are responsible for ordering calibration solutions when needed. Acceptance criteria for calibration solutions are:

- All calibration standards must be certified by the supplier to be traceable to NIST standards;
- The expiration date for each calibration standard should be no less than 90 days after receipt of the standards

The Project Manager is responsible for ensuring that calibration standards are acceptable for use.

Double blind samples are prepared by a third party laboratory and certified by that laboratory to contain constituents of concern at specified levels. Double blind samples are used to verify the accuracy of analytical results generated by EQD's contract laboratories and are purchased on an as needed basis. EQD currently obtains double blind samples from either a contractor or SP CURE. Acceptance criteria for the double blind samples are:

- Samples must be delivered to EQD on the date of intended use;
- If samples are supplied by a contractor, they must be delivered in EQD supplied bottles. These bottles must be bottles routinely used to transmit samples to the laboratories used by the Water Quality Program;
- Samples must come with a properly completed chain of custody form (if supplied by a contractor);
- Samples must be preserved in accordance with the preservation requirements of this QAPP, and;
- The certified acceptance limits for the samples must include the range of analytical results specified in the procurement documents for the sample (if supplied by a contractor).

The Project Manager is responsible for ensuring that double blind samples are acceptable for use.

Sample containers are provided by the laboratory on an as needed basis. Field Sampling Team Members are responsible for monitoring the number of sample containers available and ordering and obtaining sample containers from the WMD and contract laboratories when needed. Acceptance criteria for sample containers are:

- Sample containers must be received directly from laboratory personnel, and;
- Inspection of sample containers should reveal no visual contamination.

Additional acceptance criteria for sample containers received from contract laboratories are:

- Containers must be received in a box or other container sealed with a custody seal, and;
- Containers must be received with a certificate of compliance from the supplier. The certificate must certify that the containers have been cleaned using specified EPA cleaning procedures for low level chemical analysis

Field Sampling Team Members are responsible for verifying that sample containers are acceptable for use.

All documentation received with the items shall be maintained as quality records. Examples of these types of records include documentation related to cleanliness levels of sample containers, certified results and chain of custody forms for double blind samples.

3.8 Other Data Acquisition

In addition to the data collected under this monitoring program, data is collected or obtained from other sources for use in preparation of reports. This Section describes the data, sources from which the data are obtained, how the data are used, and what the acceptance criteria are.

3.8.1 Sampling Location Survey Data

EQD periodically uses a global positioning system (GPS) to survey sampling locations. The GPS collects data in the City standard for geographic coordinates and for elevation readings, State Plane (Colorado Central, NAD 83/92). Surveyed sample locations are uploaded into a geographic information system (GIS) and used to create graphics for reports. Locational data are also uploaded into the watershed database and are included in data downloads provided to other agencies.

EQD currently uses a Trimble® GeoXH with Terrasync Professional to survey sample locations. The Trimble® GeoXH receiver records positions with subfoot accuracy. More information on the Trimble® GeoXH can be found at the Trimble web page.

Surveyed sample location data are not used for making regulatory decisions and as a result, no additional quality requirements are necessary.

3.8.2 Stream Flow Data

EQD routinely uses stream flow data from other sources to help in the analysis of data collected as part of the water quality program. Data is acquired from the USGS or the Colorado Division of Water Resources (CDWR) and comes from one of five sites on either Cherry Creek or the South Platte River (Table 3-9). Information on how these two agencies collect surface water flow data can be found at web sites maintained by the USGS Water Resources Program and the CDWR. Since the data are not used for making regulatory decisions no additional quality requirements are needed.

3.8.3 Other Data

EQD periodically acquires and uses other data (such as meteorological data, non-water quality related GIS data, or background information on discharges) that is not measured or generated by the Water Quality Program. This data is typically used to support data analysis or locate potential contaminant sources. The data may be used to focus future sampling efforts on specific issues, but are not used for making any regulatory decisions. Other than ensuring that the source of the data is reliable, no additional quality requirements are necessary.

3.9 Data Management

EQD collects and manages a large volume of data associated with the Water Quality Sampling Program. Data collected includes field readings, analytical results, survey data, and stream flow data. EQD receives data in both hard copy and electronic formats.

3.9.1 Sampling Calendar

EQD maintains a water quality sampling calendar which contains all of the sampling events for the current month and the next two months. The calendar is updated monthly by the

Project Managers. The calendar indicates the project(s) and number of samples to be collected and the sampling date. Actual sampling locations and analytes are kept on a shared drive on the City network. Sampling Team Members should check the list on the network drive to ensure the Project Managers have not changed sampling locations for any of the projects. Sampling Team Members are responsible for checking the sampling calendar to determine sampling requirements for the day.

The calendar is also used by the WMD Laboratory for planning to accommodate future sampling events.

3.9.2 Field Data

Field data includes readings collected in the field on portable water quality instruments, observations made at the time samples were collected, and information on sampling location, time, and date. This information is recorded on field forms (see EQD Procedures ST-004 (Using Field Forms) and LK-002 (Field Forms), Appendix A) and in a field log book.

Field forms are the official chain-of-custody form for the WMD Laboratory and are submitted to the laboratory along with the samples. The original copies of the field forms are returned to EQD with the analytical results for each sample after sample analysis is complete. This usually takes five to ten business days.

3.9.3 Analytical Results

EQD routinely receives analytical results in both hard copy and electronic format.

Hard Copies of Results
Hard copies of analytical results from the WMD Laboratory are reviewed and then manually entered into the Water Quality Database by the Data Entry Clerk. If review of the data reveals any inconsistencies, the WMD Laboratory is consulted for clarification. After the data has been entered into the Water Quality Database it is checked against the hard copy to verify data entry accuracy. Any errors are corrected. Once data is entered into the database and verified, the hard copies are filed in the water quality data files. EQD maintains hard copies of analytical data for ten years in accordance with the DEH Records Retention Policy. The WMD Laboratory maintains a copy of all field forms in the WMD files.

Electronic Data Deliverables
EQD receives electronic data deliverables (EDDs) from contract laboratories. Prior to uploading, the format of the electronic data deliverables is checked for consistency with the Water Quality Database and the results are corrected to ensure that any QA samples are properly identified. If the data is not formatted correctly, the EDD is rejected and returned to the contract laboratory for corrections. The data is then uploaded into the database. If the EDD contains any records which do not match the EQuIS data dictionary, the EDD will be rejected and returned to the contract laboratory for correction. Electronic copies of EDDs and contract laboratory data reports are maintained for as long as they are needed in accordance with the DEH Records Retention Policy.

EQD also receives electronic copies of data reports from the contract laboratory. All contract laboratory data packages will contain the following information:

- Table of contents - listing the order of the package
- Case narrative – describing sample condition upon receipt, explanations of procedure and any supplemental QA information as needed.

- Executive summary – listing detection highlights for each samples
- Methods summary – listing the parameter, analytical method and preparation method associated with sample analysis.
- Method Analyst Summary – listing the method performed and the analyst performing such
- Sample Summary – listing the laboratory work order number, the laboratory sample identification number (ID), the client sample ID, date and time sampled
- Detailed analytical reports for each parameter run on each sample including results, reporting limit, units and any qualifiers as required by the method as well as laboratory tracking information concerning lot, preparation date, preparation batch, work order, analysis date/time, dilution factor, and analytical method.
- QC Data Association Summary – listing sample preparation and analysis control numbers associated with each sample
- Detailed QC reports for every associated method blank, control samples, matrix spike/duplicate, and or lab duplicate (complete with acceptable percent recovery (%R) and / or (relative percent difference) RPD range and calculated %R and / or RPD for each parameter)
- Copy of the chain of custody form

3.9.4 Other Data

Survey Data
Survey data collected using the GPS are directly uploaded to the GIS from the GPS unit. The data are used to create GIS layers showing each location. The locations are visually verified against georeferenced aerial photographs in the GIS and then the coordinates are then exported from GIS to the Water Quality Database where they are stored in a sample location data table.

Stream Flow Data
Stream flow data is downloaded from the USGS and CWDR websites and stored in Excel spreadsheets or a Microsoft® Access database for use as needed.

3.9.5 Water Quality Databases

EQD stores all critical data associated with its water quality sampling program in a database. Data associated with stream sampling are stored in an EQuIS database and data associated with lake sampling are stored in an Access Database". Both databases allow users to enter and export data as needed. Data can be viewed in a "forms" view or can be exported for manipulation in another program by creating queries or reports based on the tables in which the data is stored.

Despite the fact that data in both databases is carefully verified after entry, errors are occasionally found. All users of the database are responsible for reporting database problems to the Data Entry Clerk. The Data Entry Clerk is responsible for checking data errors against the hard copy and making corrections to the database, if appropriate. Database maintenance issues and upgrades that cannot be addressed by the Data Entry Clerk are handled by EQD Information Technology staff or by Earthsoft, the EQuIS vendor.

Procedures for managing the databases from generation to final use and storage are detailed in subsections that follow.

Database entry
Data will not be entered into the database unless the report has been approved for entry by the Project Manager. Manual data entry will be performed by the Data Entry Clerk and verification will be performed by a Field Sampling Team Member. For the Lakes Database, verification consists of comparing the raw data to the data in the database. For the Water Quality Database, the verification will be performed in EDGE. All data with laboratory flags should also be flagged in the database. Verified data should be coded as verified in the database.

Data should be entered into the database and verified within 60 days of receipt from the laboratory.

Reporting Data
The database is designed to accommodate prompt generation of reports as needed by the Project Manager. The results of all monitoring analyses will be compared to the DQOs and to the QA objectives.

Annual reports will be prepared incorporating data generated during the specified timeframe. Annual reports will be submitted to the appropriate parties by the end of the second quarter.

Database Security and Backup
After a data package has been checked for accuracy and completeness (i.e., validated and verified), it will be added to the database. The EQuIS database is housed on a third-party data server and is backed up onto long-term storage media on a regular basis. The Lake Database is stored on a City maintained server and is also backed up onto long-term storage media a regular basis. Any back-up sets of archive disks will be stored either in a separate off-site location or locked into a fire-proof cabinet at EQD.

QA Objectives for Database Management
Data generated by this Program will be managed in computer databases. The objectives of database are:

- To be complete, accurate, up-to-date, and capable of generating data tables that are compatible with the reporting requirements of the Program;
- To permit data to be accessed quickly to accommodate the needs of the project team and any outside inquiries
- To secure data to prevent unauthorized data entry and manipulation.

3.9.6 Statistical Techniques for Data Analysis

A variety of statistical approaches may be utilized for analysis of the various projects undertaken by the Water Quality Program. All data analysis and graphical output is performed using Microsoft® Excel, Minitab (Minitab, 2013), and / or Time Trends (NIWA, 2012). While there are unique aspects to analyses within the different EQD water quality projects, there are also some common approaches.

One theme common to analyses for most water quality projects entails comparison of results to established benchmarks. Benchmarks for most parameters are based on calculation of the 85th percentile using available historical data. The 15th percentile is used for DO while both the 15th and 85th percentiles are calculated for pH. The benchmark for bacterial parameters (and *E. coli*) are based on the geometric means categorized by temperature. This approach to benchmarks is consistent with CDPHE's 303(d) listing

methodology (WQCC, 2011). Analytical approaches unique to specific projects are specified below.

Trend
EQD's trend monitoring effort is a long-term project focused on assessment of long-term trends in instream water quality and on assessing the effects of urbanization on the South Platte watershed. Objectives of analytical approaches are to:

- What progress is being made towards achieving the City's goals of attaining fishable / swimmable waters in Denver?
- Are actions taken by the City to improve water quality effective?
- Is water quality in Denver's streams improving through time?
- Are there problem areas that require attention?
- How do the upper reaches of the watershed affect the receiving waters?

Answers to these questions can be grouped into two categories – comparison to standards and assessment of trends.

Overall water quality conditions and exeedances of water quality standards will be determined by comparing results to State of Colorado Water Quality Standards (WQCC, 2014) using techniques described in WQCC (2011). The techniques described in that document can be used to determine exceedances of acute and chronic standards and will also give an assessment of overall water quality.

The answers to the rest of the questions can be obtained by an evaluation of temporal and spatial trends in water quality.

Progress towards achieving Greenprint Denver's goals of attaining fishable swimmable waters and to a demonstration of whether or not water quality is improving thorugh time will be done using graphical techniques and statistics. Box and whisker plots can be used to graphically assess trends. Statistical techniques such as the Kruskal Wallis Means Test can be used to determine if observed changes in water quality through time are significant. Trends can also be evaluated using standard nonparametric statistical techniques such as the Seasonal Kendall Test for Trend.

The presence of problem areas and determination of how the upper reaches of the watershed affect the receiving waters can all be examined by looking at spatial water quality trends.

Spatial trends are currently assessed graphically using box and whisker plots to illustrate changes in levels of analytes from upstream to downstream. Assessment of spatial trends indicates overall changes in water quality as surface waters pass through CCoD. Statistical techniques such as the Kruskal Wallis Means Test may be used to determine if differences in water quality between sites is significant.

Lakes
The EQD Lakes Assessment Program serves to ensure the well being of the lake environment and the citizens utilizing them within CCoD. Analysis of lake sampling data strives to:

- Identify exceedances of water quality standards;
- Provide meaningful input into the State's 303(d) listing processes and into TMDL development;
- Assess the overall health of lake ecosystems;
- Assess long-term trends in water quality, and;

- Provide management recommendations to the City's Parks and Recreation Department.

Standard Exceedance & 303(d) Listing Input: Water quality standard exceedances are assessed based on daily (annual) and long-term (2-5 years) data utilizing benchmarks (described in the 3.9.6 introduction) and CDPHE standards. Daily measurements merely serve as indications of temporary issues and may qualify a lake for the Monitor and Evaluation list (a list of potentially impaired waters maintained by the WQCD) until an adequate amount of long-term data can be used to evaluate exceedances meeting 303(d) listing criteria.

Lake Ecosystem & Long-Term Trends: To assess general conditions, results are compared with the 85th percentile (and 15th percentile for pH and DO) of yearly data from all Denver Lakes and also with long term data. The Carlson Trophic Status Index is calculated based on chlorophyll-a, secchi depth, and total phosphorous results. A variety of graphical approaches are also used to assess and present the results.

Management Recommendations: Results are compared to appropriate sediment and water quality criteria and/or standards to determine potential issues involving renovation or site assessment. While there are few analyses necessary for this assessment, the nutrient related parameters are assessed as a group (nitrogen, phosphorous, secchi depth, chlorophyll-a) to determine factors driving eutrophication.

Monitoring of High Use Areas
EQD conducts routine monitoring of bacteria levels in at a number of sampling location in the City from mid-May through October. The results of these findings are compared with CDPHE Natural Swim Beach water quality standards (CDPHE, 1998) to determine whether there is a need to alert the public. Because the testing is an evaluation of acute exposure to pathogens, there is no need for statistical analyses for these purposes.

Other Sampling Initiatives
In addition to routine monitoring activities and special projects, EQD monitors other locations on an as needed basis. Examples of such projects include determining the impact of BMPs on water quality, one-time spills, or discharges and in response to citizen complaints. The analysis of data generated from these efforts will vary from project to project, but generally it will strive to:

- Provide environmental and public health oversight;
- Determine compliance with TMDLs or permit requirements, and;
- Enforce local, state, and federal water quality ordinances and regulations as appropriate.

Statistical analyses for other sampling initiatives are determined on a project-by-project basis and are documented in the SAP / QAPP for each project.

Table 3-1 Project Analytical Suites

Project		Field	Nutrient	Solids / Cations	Organic Carbon	Bacteria	Anions / Metals	VOC /SVOC	Other
Trend									
	Cherry Creek / South Platte River	X	X	X	Diss	X	Diss / Tot / TREC	-	-
	Tributaries	X	X	X	Diss	X	Diss / Tot / TREC	-	-
Lakes	Water	X	X	TSS / TDS	Diss	X	PD / Tot	+	+
	Sediment	X	X	-	Tot	-	Tot	+	+
High Use Areas		X	-	-	-	X	-	-	-
Other Sampling Initiatives		X	+	+	+	+	+	+	+

Notes:

X Analyses performed
- Analyses not performed
+ As needed
TBD To be determined

Analytical Suites:

Field: pH, Temperature, Dissolved Oxygen, Specific Conductivity

Nutrients: Total Ammonia, Nitrite, Nitrate, Total Kjeldahl Nitrogen, and Total Phosphorous
- Lake samples also analyzed for Ortho Phosphate

Solids / Cations: Alkalinity, Hardness, Chloride, Sulfate, Total Dissolved Solids, Total Suspended Solids.
- Alkalinity, and hardness analyses generally only performed if sample is also analyzed for metals

Bacteria: *E. coli*, fecal coliform

Anioins / Metals: Aluminum, Arsenic, Cadmium, Chromium, Copper, Iron, Lead, Manganese, Mercury, Molybdenum, Nickel, Selenium, Silver, Uranium, and Zinc. Others as required by project needs
- Diss = dissolved
- PD = potentially dissolved
- Tot = total
- TREC = total recoverable

VOC\SVOC: Standard suite from EPA Methods 8260 or 8270 and 1,4-Dioxane if required

Table 3-2 Sampling Frequency

Project		**Sampling Frequency**	**Duration**
Trend			
	Cherry Creek, South Platte River	Monthly	Year Round
	Bear Creek, Harvard Gulch West, Harvard Gulch, Sanderson Gulch, Weir Gulch, Lakewood Gulch, Goldsmith Gulch, Westerly Creek	Quarterly	Year Round
Lakes		Annually	Mid-Summer
High Use Areas			
	Confluence Park, Bear Creek Park	Once a week from	May 1 through Oct. 1
	Sloans Lake	Every two weeks from	Late-April through mid-Oct.
	Westerly Creek, Cherry Creek at Holly, Rocky Mountain Lake, Berkeley Lake	Minimum of once a month	May 1 through Oct. 1
	Other Sites	As needed	May 1 through Oct. 1
Other Sampling Initiatives		TBD	

Table 3-3 Analytical Detection Limit Requirements

Analyte	Water			Sediment		
	Units	Standard / Criteria	Required RL	Units	Criteria / Guidance[1]	Required RL
Alkalinity	mg/L	-	5.0			
Hardness	mg/L	-	5.0			
E. coli	CFU / 100 mL	126	10			
Total Organic Carbon	mg/L	-	2.0	mg/kg	-	2.0[2]
Dissolved Organic Carbon	mg/L	-	2.0			
Total Ammonia	mg/L	0.018[3]	0.10	mg/kg	-	2.0[2]
Nitrite	mg/L	0.5	0.10	mg/kg	-	-[5]
Nitrate	mg/L	2.01 / 0.91[6]	0.2	mg/kg	-	0.5[2]
Total Kjeldahl Nitrogen	mg/L	-	1.00	mg/kg	-	200[2]
Total Phosphorous	mg/L	0.17 / 0.083[6]	0.08	mg/kg	-	15[2]
Ortho Phosphorous	mg/L	-	0.5			
Chloride	mg/L	250[7]	6			
Sulfate	mg/L	250[7]	50			
Total Dissolved Solids	mg/L	-	10			
Total Suspended Solids	mg/L	-	40			
Chlorophyll-a				ug/L		1.0
Total Solids				%	-	0.1
Total Volatile Solids				%	-	0.1
Percent Moisture				%	-	0.1
Aluminum	ug/L	87	50	ug/kg	-	10
Arsenic	ug/L	0.02	0.4[4]	ug/kg	33	1.0
Cadmium	ug/L	0.25[8]	0.1	ug/kg	3.2	
Chromium	ug/L	42[8]	2.0	ug/kg	111	1
Copper	ug/L	5.0[8]	2.0	ug/kg	100	2
Iron	ug/L	1000(trec) / 300(diss)	100	ug/kg	250000	10
Lead	ug/L	1.2[8]	0.4	ug/kg	82	0.8
Manganese	ug/L	50[7]	10	ug/kg	1200	1
Mercury	ug/L	0.01 (tot)	0.01	ug/kg	1.1	33
Nickel	ug/L	29[8]	2.0	ug/kg	33	4
Selenium	ug/L	4.6	1.0	ug/kg	-	1.3

Table 3-3 Analytical Detection Limit Requirements (cont.)

Analyte	Water			Sediment		
	Units	Standard / Criteria	Required RL	Units	Criteria / Guidance[1]	Required RL
Silver	ug/L	0.10[8]	0.05	ug/kg	-	1
Uranium	ug/L	30[7]	10	ug/kg	-	20
Zinc	ug/L	65[8]	20	ug/kg	459	2
VOCs	ug/L	See WQCC (2012)	25% of Std	ug/kg	EPA (2004a, Table C-1)[9]	25% of Guidance
SVOCs	ug/L	See WQCC (2012)	25% of Std	ug/kg	EPA (2004a, Table C-1)[9]	25% of Guidance

Notes:

RL Reporting Limit

- No standard or criteria for this analyte.

1 Based on the more conservative of the values from: EPA (2001c) Probable Effect Concentration (arsenic, chromium, mercury, and zinc) or EPA (2002d) Probable Effect Level (cadmium, copper, iron, manganese, lead, and nickel).

2 Based on previously reported values.

3 Ammonia standard calculated using formulas presented in WQCC (2012) and is based on a pH of 9 and temperature of 30° C.

4 Based on existing method reporting limit.

5 Sediment samples are analyzed for nitrite + nitrate.

6 Standards for nitrogen and phosphorous have delayed implementation dates of May 31, 2017 and May 31, 2022 respectively. The first value is for streams, the second value is for lakes.

7 Drinking water standard.

8 Metals standards calculated using formulas presented in WQCC (2012). Listed standards are based on hardness of 50.

9 Appendix C, Table C-1, ESG or C_{oc} Tier 2; ESG = Equilibrium Partitioning Sediment Guideline, C_{oc} = Effect Concentration (in sediment)

Samples not analyzed for this parameter.

Table 3-4 Analytical Methods, Containerization, and Preservation Requirements

Analyte	Method	Container	Preservative	Hold Time	Reference
Field Readings					
pH	Field	N/A	N/A	N/A	WQ-001 (Appendix 2)
Temperature	Field	N/A	N/A	N/A	WQ-001 (Appendix 2)
Dissolved Oxygen	Field	N/A	N/A	N/A	WQ-001 (Appendix 2)
Specific Conductivity	Field	N/A	N/A	N/A	WQ-001 (Appendix 2)
Turbidity	Field	N/A	N/A	N/A	WQ-001 (Appendix 2)
Aqueous					
Alkalinity	SM 2320B	(1) 1-L poly	Cool to 4° C	14 days	APHA (2005)
Hardness	SM 2340C	[1]	Cool to 4° C	6 months	APHA (2005)
E.Coli	SM 9222	(1) Whirl-pak	Cool to 4° C	6 hrs	APHA (2005)
Total organic carbon	SM 5310C	(1) 40-mL glass vial	Cool to 4° C	7 days	APHA (2005)
Dissolved organic carbon	SM 5310C	(1) 40-mL glass vial	Filter, Cool to 4° C	7 days	APHA (2005)
Total Ammonia	SM 4500-NH_3-G	(1) 1-L poly	Cool to 4° C, H_2SO_4 to pH < 2	7 days	APHA (2005)
Nitrite	SM 4500-NO_2^-B	[1]	Cool to 4° C	48 hrs	APHA (2005)
Nitrate	SM 4500-NO_3^-F	[1]	Cool to 4° C	48 hrs	APHA (2005)
Total Kjeldahl Nitrogen	SM 4500-N_{ORG} B + NH_3	[3]	Cool to 4° C, H_2SO_4 to pH < 2	7 days	APHA (2005)
Total Phosphorous	SM 4500-P B5 + F	[3]	Cool to 4° C, H_2SO_4 to pH < 2	28 days	APHA (2005)
Ortho Phosphate	SM 4500-P B5 + G	[3]	Cool to 4° C, H_2SO_4 to pH < 2	48 hrs	APHA (2005)
Chloride	SM 4500-Cl^-	[1]	Cool to 4° C	28 days	APHA (2005)
Sulfate	SM 4500-SO_4^{2-}	[1]	Cool to 4° C	28 days	APHA (2005)
TDS	SM 2540 C	[1]	Cool to 4° C	7 days	APHA (2005)
TSS	SM 2540 D	[1]	Cool to 4° C	7 days	APHA (2005)
Chlorophyll-a	Ethanol extraction; spectrophotometric	(1) 1-gal wrapped (or amber) glass	Cool to 4° C	4hrs	Lewis and Saunders 1985, CDPHE 1993
Metals, Dissolved	EPA 200.8 or 200.7	(1) 500-mL poly	Cool to 4° C, filter, HNO_3 to pH <2	6 months	EPA (2000b)
Mercury, Dissolved	EPA 245.1	[4]	Cool to 4° C	28 days	EPA (1994b)
Metals, Total	EPA 200.8 or 200.7	(1) 500-mL poly	Cool to 4° C w/ HNO_3 to pH <2	6 months	EPA (2000b)
Mercury, Total	EPA 245.1	[4]	Cool to 4° C w/ HNO_3 to pH <2	28 days	EPA (1994b)
Metals, Potentially Diss	EPA 200.8 or 200.7	(1) 500-mL poly	Cool to 4° C w/ HNO_3 to pH <2	6 months	EPA (2000b)
Mercury, Potentially Diss	EPA 245.1	[4]	Cool to 4° C w/ HNO_3 to pH <2	28 days	EPA (1994b)
Metals, Total Recoverable	EPA 200.8 or 200.7	(1) 500-mL poly	Cool to 4o C w/ HNO3 to pH <2	6 months	EPA (2000b)
Mercury, Total Rec	EPA 245.1	[4]	Cool to 4o C w/ HNO3 to pH <2	28 days	EPA (1994b)
VOCs	EPA 8260B	(3) 40 mL VOA vials	Cool to 4o C w/ HCl to pH <2	7 days	EPA (2000b)
SVOCs	EPA 8270C	(1) 80 oz amber	Cool to 4o C	5 days	EPA (2000b)

Table 3-4 Analytical Methods, Containerization, and Preservation Requirements (cont.)

Analyte	Method	Container	Preservative	Hold Time	Reference
Sediment					
Ammonia	EPA 350.1	8-oz wide mouth jar	Cool to 4° C	28 days	EPA (1983)
Nitrite + Nitrate	EPA 353.2	5	Cool to 4° C	28 days	EPA (1983)
Total Kjeldahl Nitrogen	EPA 351.2	5	Cool to 4° C	28 days	EPA (1983)
Total Phosphorous	EPA 365.3	5	Cool to 4° C	28 days	EPA (1983)
Total Organic Carbon	EPA 9060	5	Cool to 4° C	28 days	EPA (2000b)
Total Solids	EPA 160.3	5	Cool to 4° C	7 days	EPA (1983)
Percent Moisture	EPA 160.3 MOD	5	Cool to 4° C	N/A	EPA (1983)
Total Volatile Solids	EPA 160.4	5	Cool to 4° C	7 days	EPA (1983)
Metals, Total	EPA 6010B	(1) 4 oz WM jar	Cool to 4° C	6 months	EPA (2000b)
Mercury, Total	EPA 7471A	6	Cool to 4° C	28 days	EPA (2000b)
VOCs	EPA 8260B	(1) 4 oz WM jar	Cool to 4° C	14 days	EPA (2000b)
SVOCs	EPA 8270C	(1) 4 oz WM jar	Cool to 4° C	14 days	EPA (2000b)
Total Kjeldahl Nitrogen	EPA 351.2	5	Cool to 4° C	28 days	EPA (1983)
Total Phosphorous	EPA 365.3	5	Cool to 4° C	28 days	EPA (1983)

Notes:

N/A Not applicable, reading collected from instream or lake sampling locations or no hold time.

1 Collected in same container as alkalinity sample.

2 Collected in same container as *E. coli* sample.

3 Collected in same container as total ammonia sample.

4 Collected in same container as other metals samples with same analysis type (i.e. totals with totals, potentially dissolved with potentially dissolved, etc.).

5 Collected in same container as other sediment nutrients.

6 Collected in same container as other sediment metals.

Table 3-5 Meters Currently Used for Stream, Outfall, and Lake Water Quality Sampling

Meter	Parameters Measured[1]	Date Purchased	Status[2]
Horiba U-52	pH, temp, cond, DO, TDS, turbidity	October 2012	A
YSI ProPlus	pH, temp, cond, DO, TDS, salinity	2009/2010	B
YSI-556 Multi-meter (B)	pH, temp, cond, TDS, salinity	July 2004	B
Hach 2100P	Turbidity	2001	C
YSI-ProDO	DO, temp	2009/2010	C

Notes:
Table does not include meters that are in dry storage.
1 temp = temperature, DO = dissolved oxygen; cond = conductivity and specific conductivity; TDS = total dissolved solids
2 A = preferred meter for all parameters; B = second most preferred; C = backup meters

Table 3-6 Non-Meter Equipment Currently Used by EQD for Lake Sampling

Equipment	Purpose	Storage Location
John boat	Access lakes	Parks Forestry Yard – Huron St.
Boat trailer	Boat transportation	Parks Forestry Yard – Huron St.
Beta-bottle (Wildco)	Collect water samples	EQD laboratory
Eckman dredge (Wildco)	Collect sediment samples	EQD laboratory
Trolling motor	Power boat	EQD laboratory
12V battery	Power boat	EQD laboratory
Depth finder	Determine lake depths	EQD laboratory
Secchi disc	Assess water clarity	EQD laboratory

Table 3-7 Meter Calibration, Inspection, and Maintenance Activities

Meter	*Activity*	*Respons. Person*	*Frequency*	*Acceptance Criteria*	*Corrective Action*	*Relevant Reference (SOP, Tech. Support)*
Horiba U-52	Calibration	FSTM[1]	Every use	See MCM[2] Log Book	1) Re-calibrate 2) Contact tech support	
Multi-meter	Inspection	FSTM	Every use	See MCM Log Book	1) Re-calibrate 2) Contact tech support	
	General maintenance	FSTM	Every use	See manual[3]	1) Clean Probes	
		FSTM	As needed	See manual	1) In-house repair 2) Contact tech support 3) Outside repair	Manufacturer's manual and MCM Log; Geotech (303) 320-4764
	Specific maintenance: 1) Change out DO probe cap and solution; 2) replace solution in reference electrode 3) Inspect other probes	FSTM	Every two months	No bubbles in solution; no leakage; gaskets intact	1) Re-insert or replace probe-cap; 2) replace cracked or broken gaskets	
YSI-ProPlus	Calibration	FSTM	Every use	See MCM Log Book	1) Re-calibrate 2) Contact tech support	
Multi-meter	Inspection	FSTM	Every use	See MCM Log Book	1) Re-calibrate 2) Contact tech support	
	General maintenance	FSTM	Every use	See manual	1) Clean Probes	
		FSTM	As needed	See manual	1) In-house repair 2) Contact tech support 3) Outside repair	Manufacturer's manual and MCM Log; Geotech (303) 320-4764
	Specific maintenance: 1) Change out DO probe cap and solution; 2) Inspect other probes	FSTM	Monthly	No bubbles in solution; no leakage; gaskets intact	1) Re-insert or replace probe-cap; 2) replace cracked or broken gaskets	

Table 3-7 Meter Calibration, Inspection, and Maintenance Activities (cont.)

Meter	***Activity***	***Respons. Person[4]***	***Frequency***	***Acceptance Criteria***	***Corrective Action***	***Relevant Reference (SOP, Tech. Support)***
YSI-556(A)	Calibration	FSTM	Every use	See MCM Log Book	1) Re-calibrate 2) Contact tech support	Manufacturer's manual and MCM Log; Geotech (303) 320-4764
Multi-meter	Inspection	FSTM	Every use	See MCM Log Book	1) Re-calibrate 2) Contact tech support	
	General maintenance	FSTM	Every use	See manual	1) Clean probes	
		FSTM	As needed	See manual	1) In-house repair 2) Contact tech support 3) Outside repair	
	Specific maintenance: 1) Change out DO probe cap and solution; 2) Inspect other probes	FSTM	Weekly-monthly depending on amount of use	No bubbles in solution; no leakage; gaskets intact	1) Re-insert or replace probe-cap; 2) replace cracked or broken gaskets	
Calibration Standards (pH 7 and 10, conductivity 1413 uS/cm, turbidity <0.1, 20, 100, NTU)	Maintenance: Assure adequate supplies	FSTM	Replace at least once a month or more frequently depending on use	At least one month of supplies	1) Order more standard	pH, conductivity: Geotech (303) 320-4764; http://www.geotechenv.com/ Turbidity: Hach (800) 227-4224 http://www.hach.com/

Notes:
Table only includes meters which are in regular use.
1 FSTM = Field Sampling Team Member
2 Meter Calibration and Maintenance Log book, located near meters in Benthic Laboratory
3 All meter manuals are in the file in the Benthic Laboratory
3 Replace U-52 DO probe cap and solution every two month and YSI-556 DO probe cap and solution monthly at a minimum

Table 3-8 Equipment (Non-Meter) Inspection and Maintenance Activities

Equipment	Activity	Respons. Person[1]	Frequency	Acceptance Criteria	Corrective Action	Relevant Reference (SOP, Tech. Support)[2]
John boat	Annual Inspection & Maintenance	FSTM	Annual (early May)	Intact with adequate anchor and water drain, key to lock, 2 plugs	1) arrange for repairs with fleet maintenance as needed; 2) replace anchor and/or anchor line as needed; 3) purchase new plug	
Boat trailer	Annual Maintenance & Inspection	FSTM	Annual	Fleet approval	n/a	
Trolling motor	Annual Inspection and Maintenance	FSTM	Annual (May/ June)	Functional, clear of vegetative matter	1) clean and repair as needed	Fleet Maintenance - Huron
12V battery	Annual Inspection and Maintenance	FSTM	Annual (May/ June); dis-charge battery quarterly	Battery intact with adequate amount of distilled water in cells	1) maintain water level in cells w/distilled water; 2) use battery quarterly with complete discharge and recharge (fleet maintenance-Central Platte Campus) in May/June	
Beta-bottle (Wildco)	Annual Inspection, Calibration, and Maintenance	FSTM	Annual (May/ June)	No loose bolts; gaskets, pull cables, and cord intact; accurate and discernable labeling on line	1) tighten all bolts and nuts; 2) replace degraded components; 3) measure and re-new length markings	Manufacturer's manual[1]; Wildco (800) 799-8301
	Regular Inspection and Maintenance	FSTM	Prior to use & during equipment decon	No loose bolts; gaskets, pull cables, & cord intact;	1) tighten all bolts and nuts; 2) replace and/or inform AP of degraded components	

Table 3-8 Equipment (Non-Meter) Inspection and Maintenance Activities (cont.)

Equipment	Activity	Respons. Person[1]	Frequency	Acceptance Criteria	Corrective Action	Relevant Reference (SOP, Tech. Support)[2]
Eckman dredge (Wildco)	Annual Inspection and Maintenance	FSTM	Annual (May/ June)	No loose bolts; pull cables intact	1) tighten all bolts and nuts; 2) replace degraded components	
	Regular Inspection and Maintenance	FSTM	Prior to use & during equipment decon	No loose bolts; pull cables intact	1) tighten all bolts and nuts; 2) replace and/or inform AP of degraded components	
Depth finder	Annual Inspection and Maintenance	FSTM	Annual (May/ June)	Cable ends with adequate space for connection	1) cut back wire housing to allow adequate length for battery connection	Manufacturer's Manual[1]; Hummingbird Tech support at (800) 633-1468 or (344) 687-0503
Secchi disc	Annual Inspection and Maintenance	FSTM	Annual (May/ June)	Knot is taught; length de-marcations are accurate & legible	1) solidify knot; 2) calibrate and reinforce length demarcations.	n/a
Nitrile gloves	Maintenance	FSTM	As needed	Assure adequate supply of all sizes	1) order replacements when down to one month supply of any size.	Lab Safety Supplies
Sulfuric acid	Maintain adequate supply for future sampling	FSTM	Daily as samples collected	Ensure adequate supply for next sample event	1) request DWM Lab personnel to refill container, or 2) inform following sampler(s) of short-supply	DWM lab (303) 446-3827

Table 3-8 Equipment (Non-Meter) Inspection and Maintenance Activities (cont.)

Equipment	Activity	Respons. Person[1]	Frequency	Acceptance Criteria	Corrective Action	Relevant Reference (SOP, Tech. Support)[2]
Water sample bottles	Maintain adequate number of bottles in truck and in lab from contract lab	FSTM				
	Streams/outfalls:	FSTM	Daily as samples collected	Ensure adequate supply for next sample event	1) pick up bottles at DWM Lab or Contract lab, or 2) let project manager and/or personnel responsible for next sample event know of bottle needs	DWM lab (303) 446-3827 TestAmerica (303) 736-0110
	Lakes:	FSTM	Daily as sample	Assure adequate supply for next sample event	1) pick up bottles at DWM Lab or Contract lab, or 2) let project manager and/or personnel responsible for next sample event know of bottle needs	
Syringe Tip Filters	Maintain adequate supply of filters for future sampling	FSTM	Daily as samples collected	Ensure adequate supply for at least one month's sampling	Let project manager know of filter needs	

Notes
1 FSTM = Field Sampling Team Member
2 All equipment manuals are stored in the file cabinet in the Benthic Laboratory near the door.

Table 3-9 Surface Water Flow Stations and Data Sources

Station Name	Data Source	Notes
Cherry Creek Below Cherry Creek Lake	CDWR	
Cherry Creek at Glendale	USGS	Readings discontinued in 2003
Cherry Creek at Denver	USGS	At Champa
South Platte River at Englewood	USGS	At Dartmouth
South Platte River at Denver	CDWR	At 19th Street

Notes:
CDWR Colorado Division of Water Resources
USGS US Geological Survey

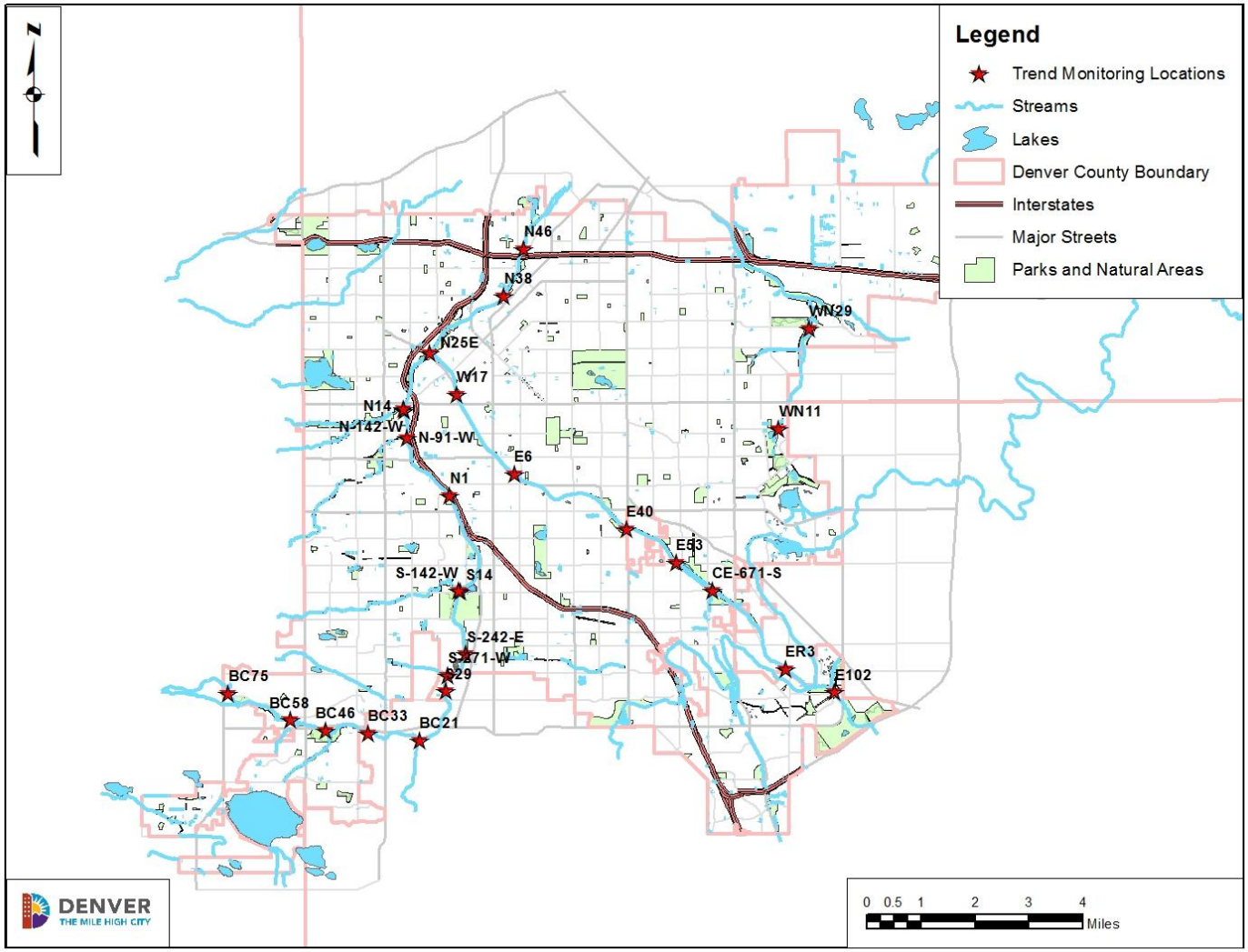


Figure 3-1 Trend Sampling Locations

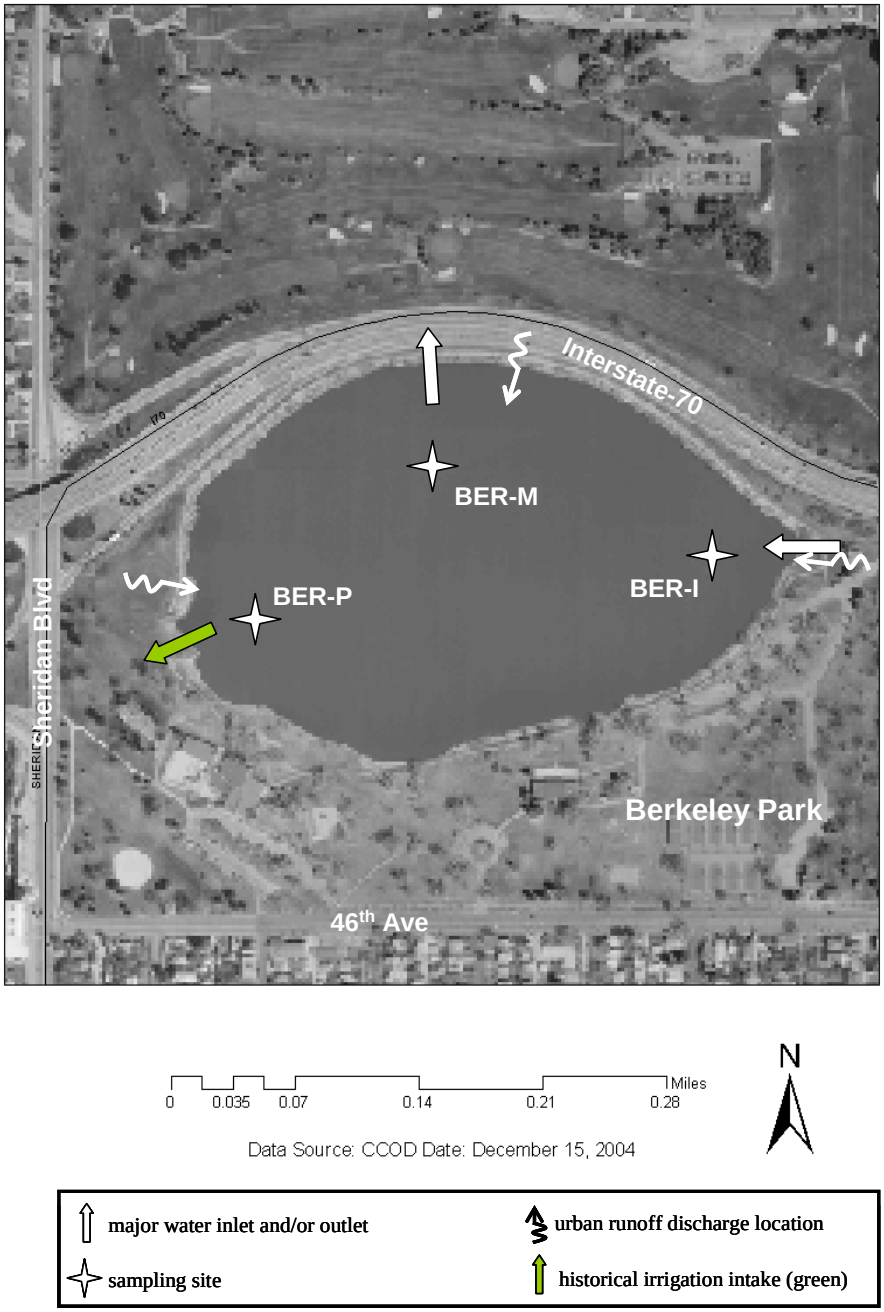


Figure 3-2 Berkeley Lake Sampling Locations

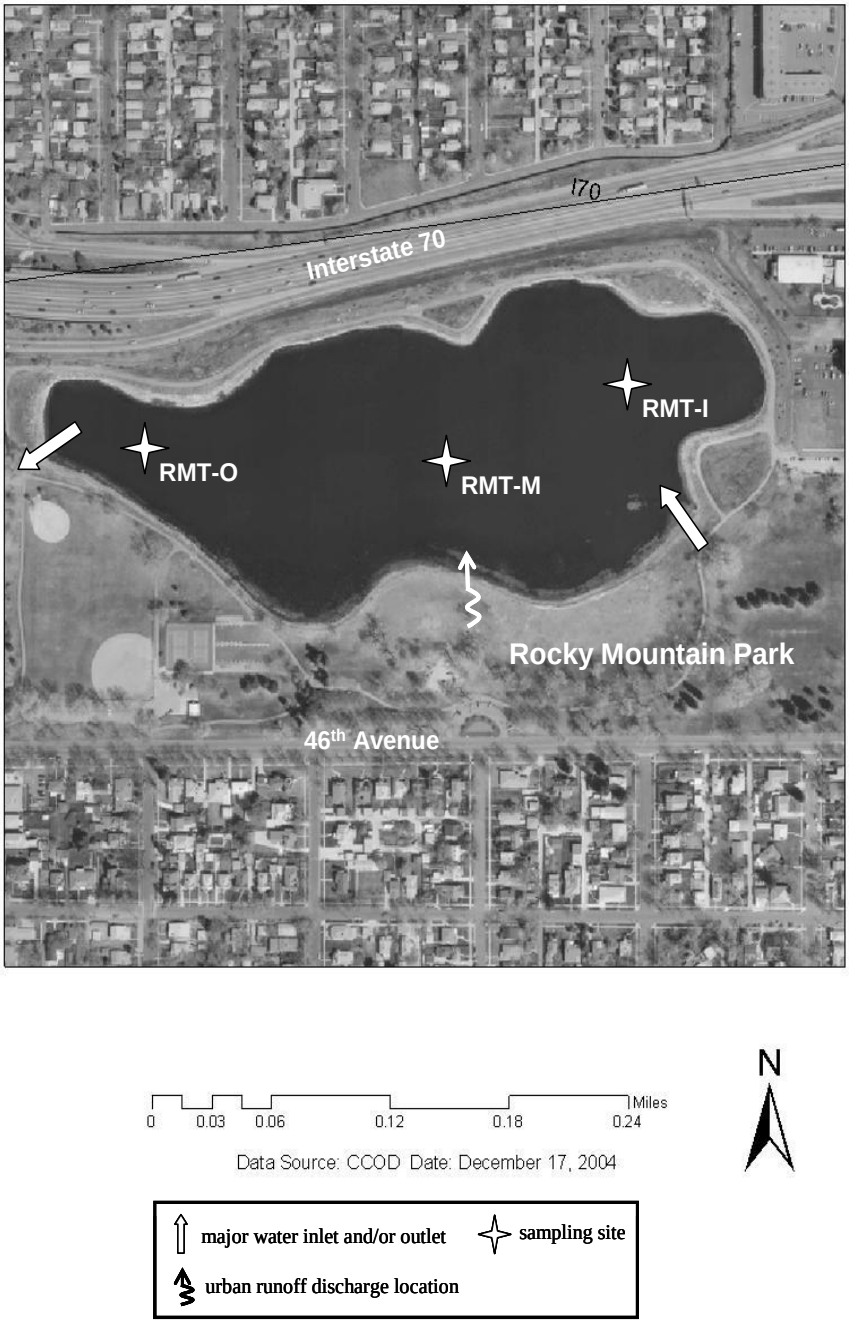


Figure 3-3 Rocky Mountain Lake Sampling Locations

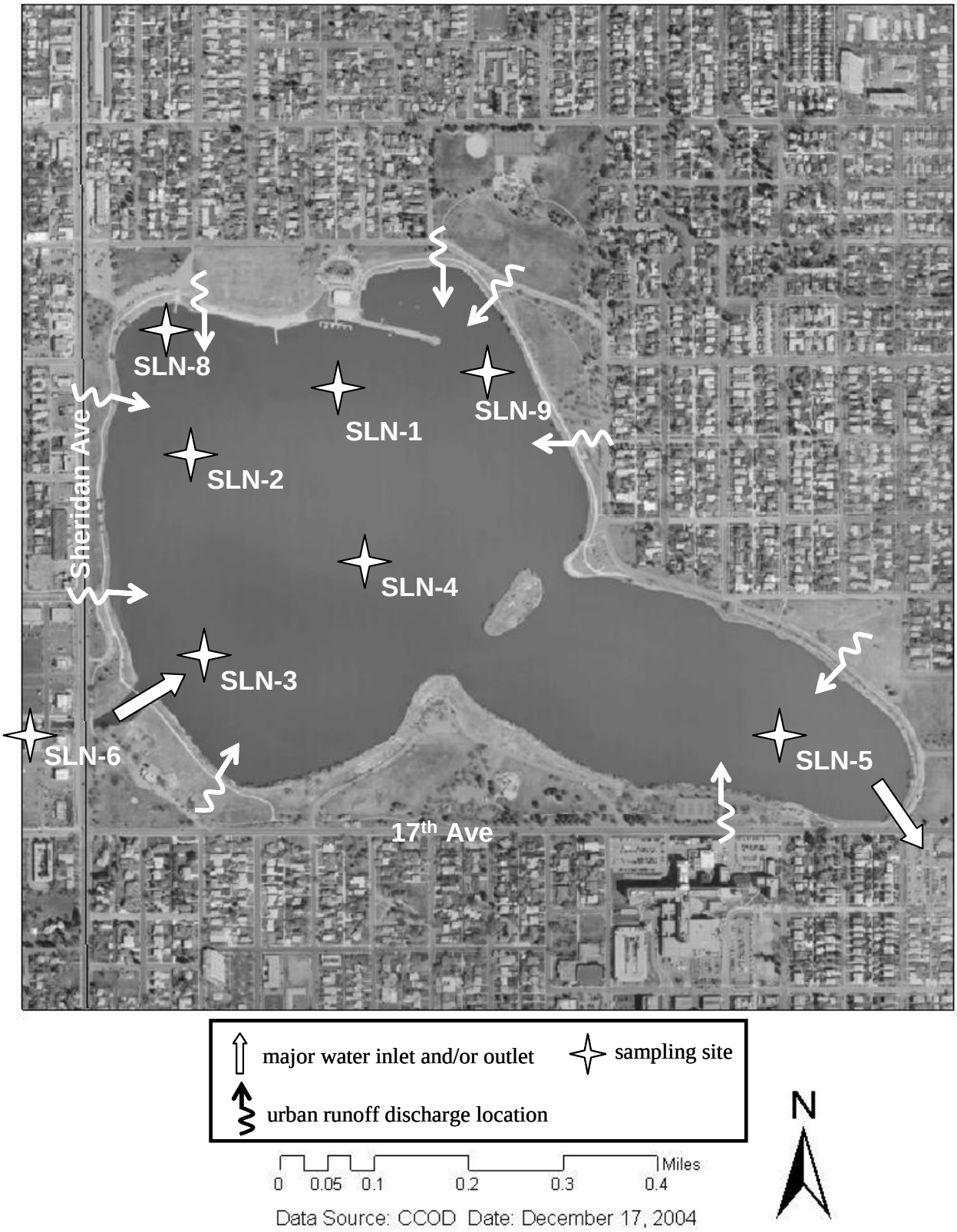


Figure 3-4 Sloans Lake Sampling Locations

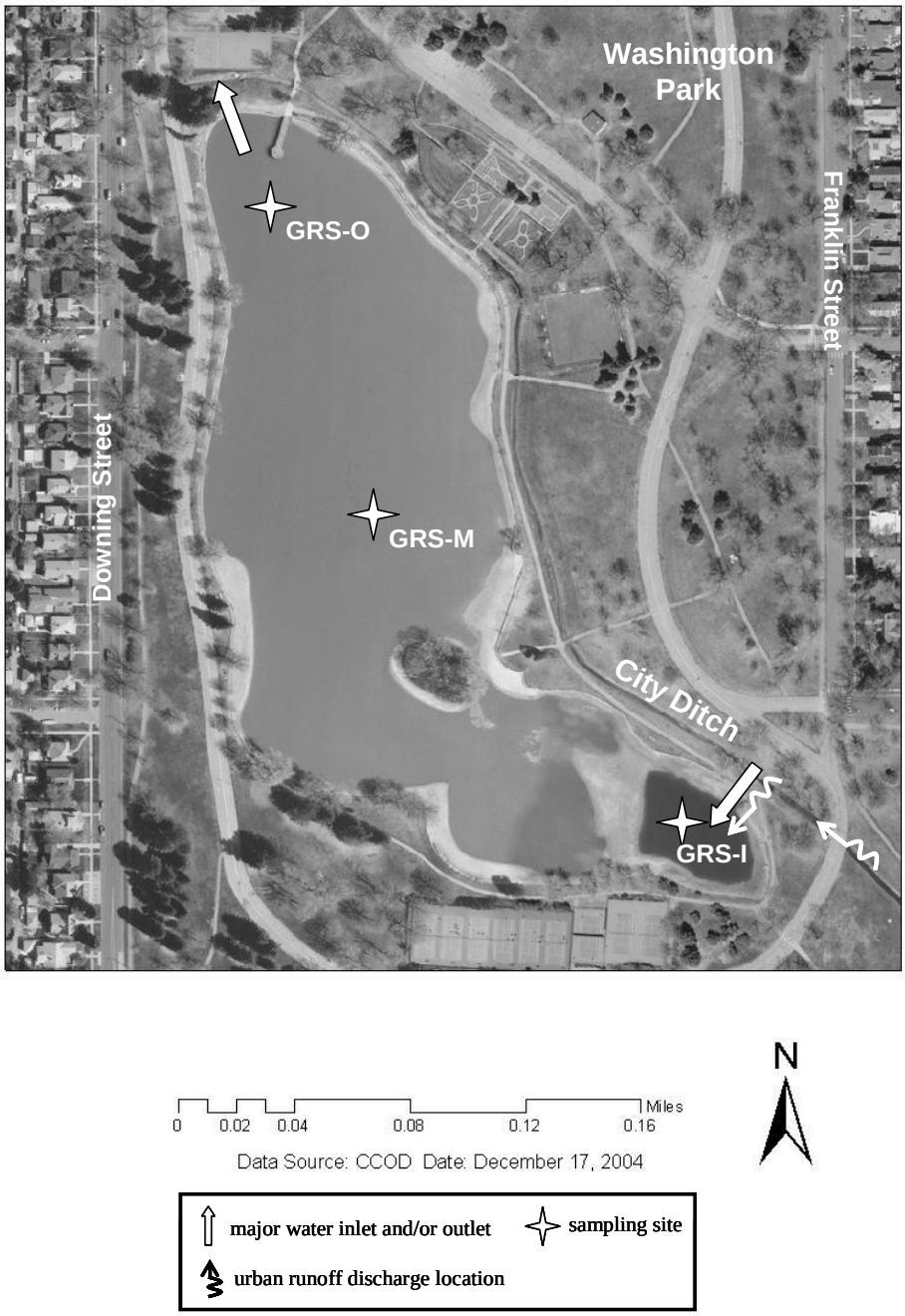


Figure 3-5 Grasmere Lake Sampling Locations

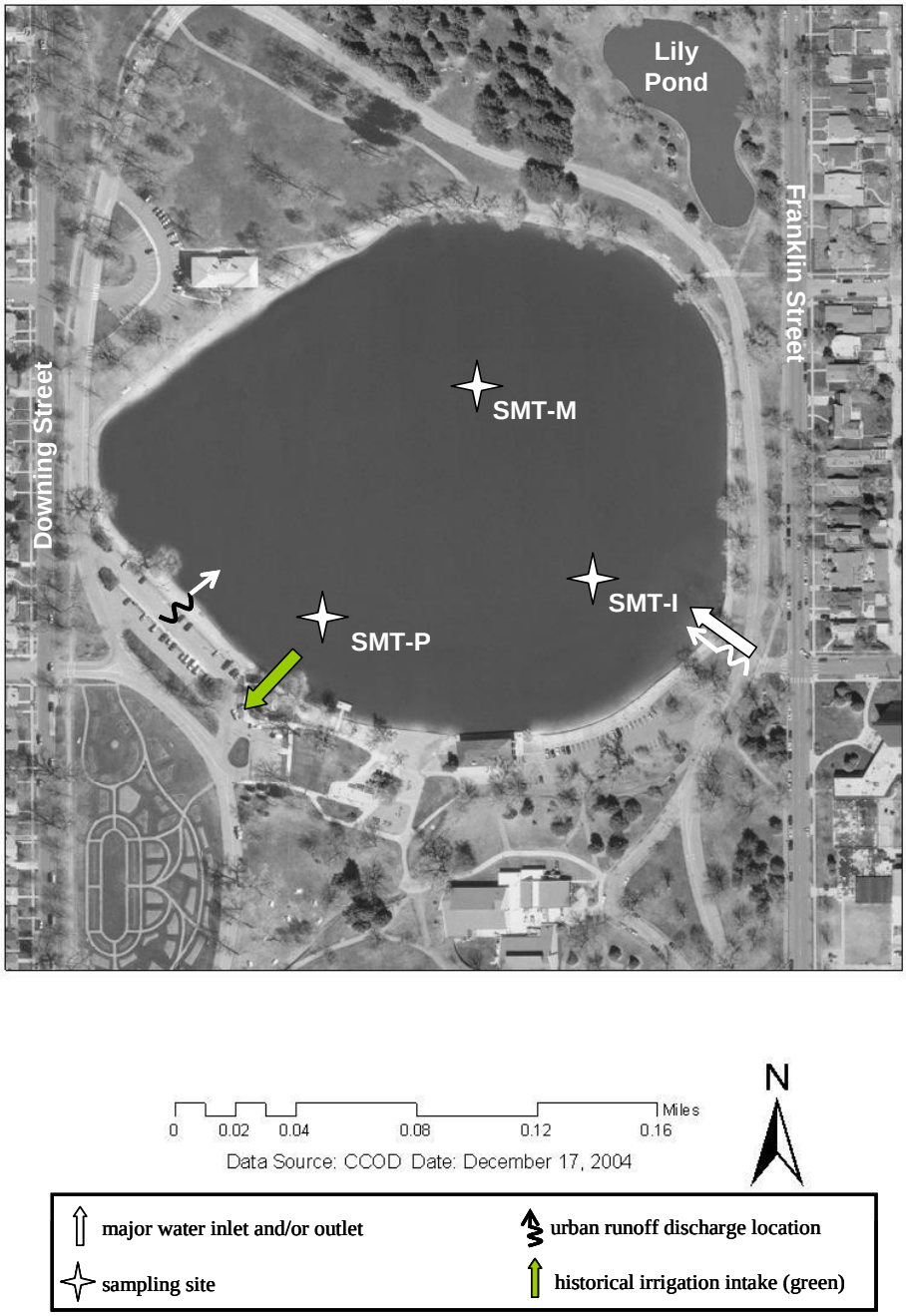
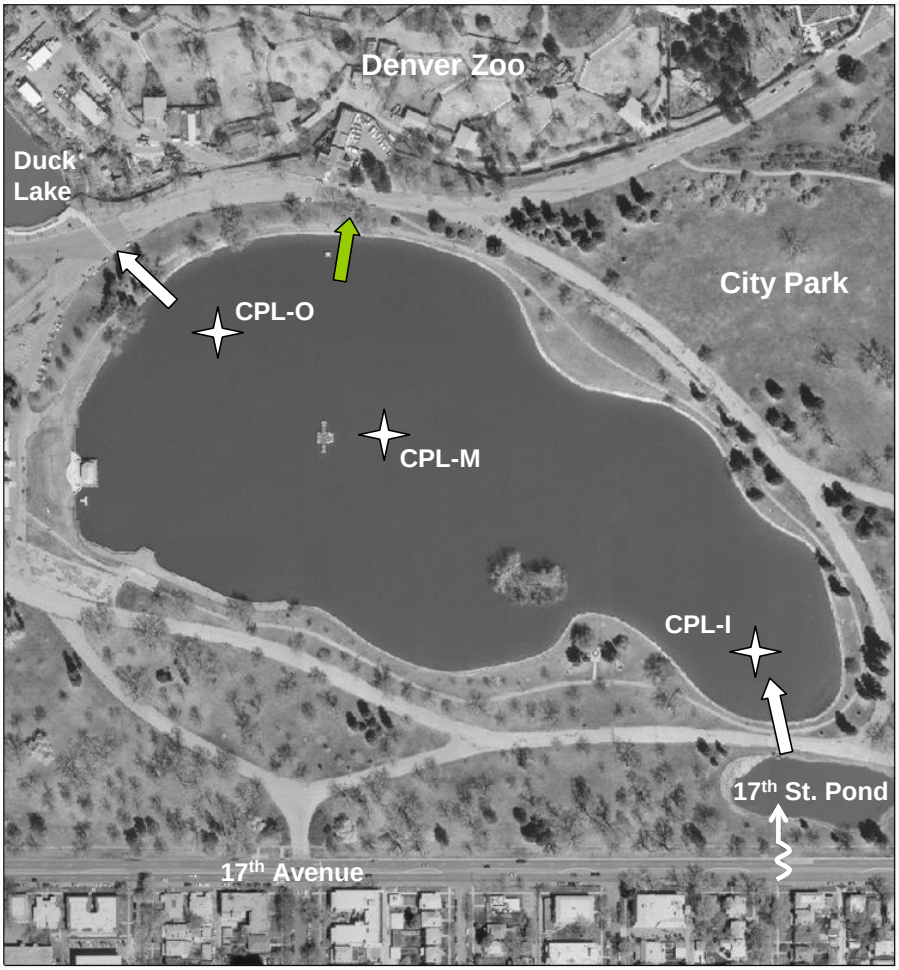


Figure 3-6 Smith Lake Sampling Locations



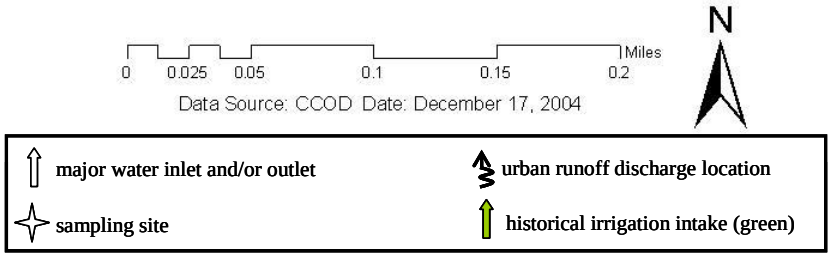


Figure 3-7 Ferrill Lake Sampling Locations

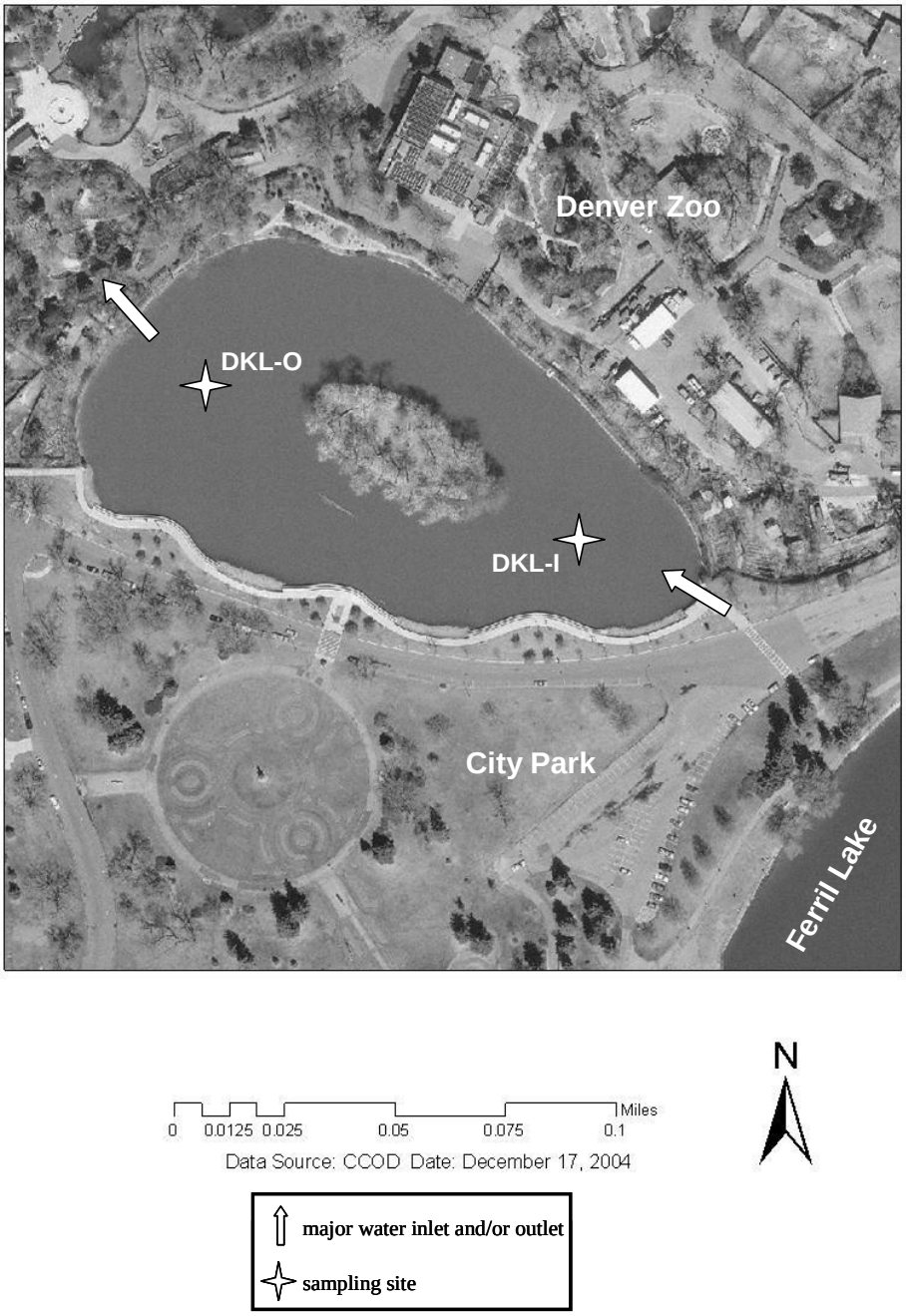
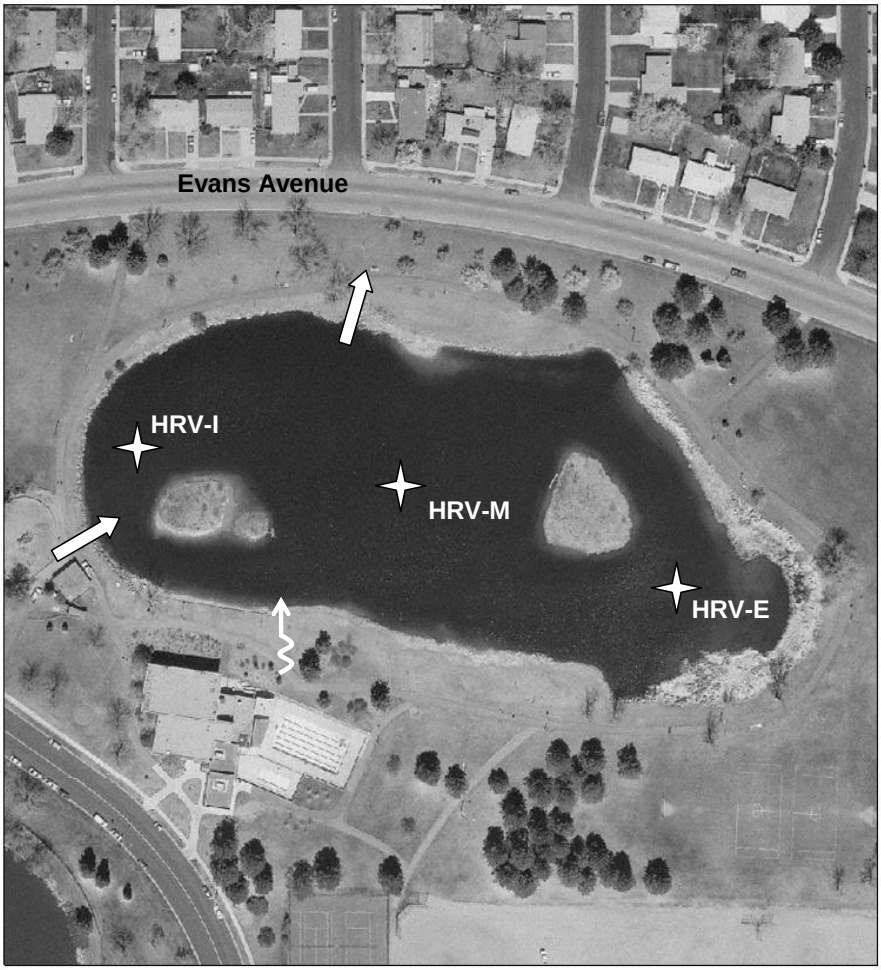


Figure 3-8 Duck Lake Sampling Locations



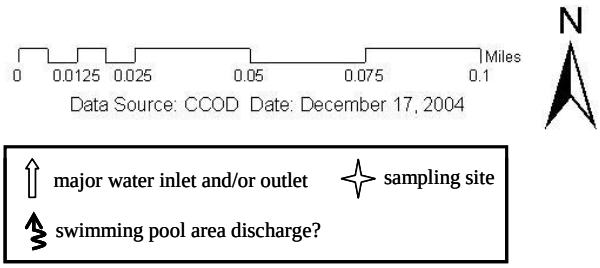


Figure 3-9 Harvey Lake Sampling Locations

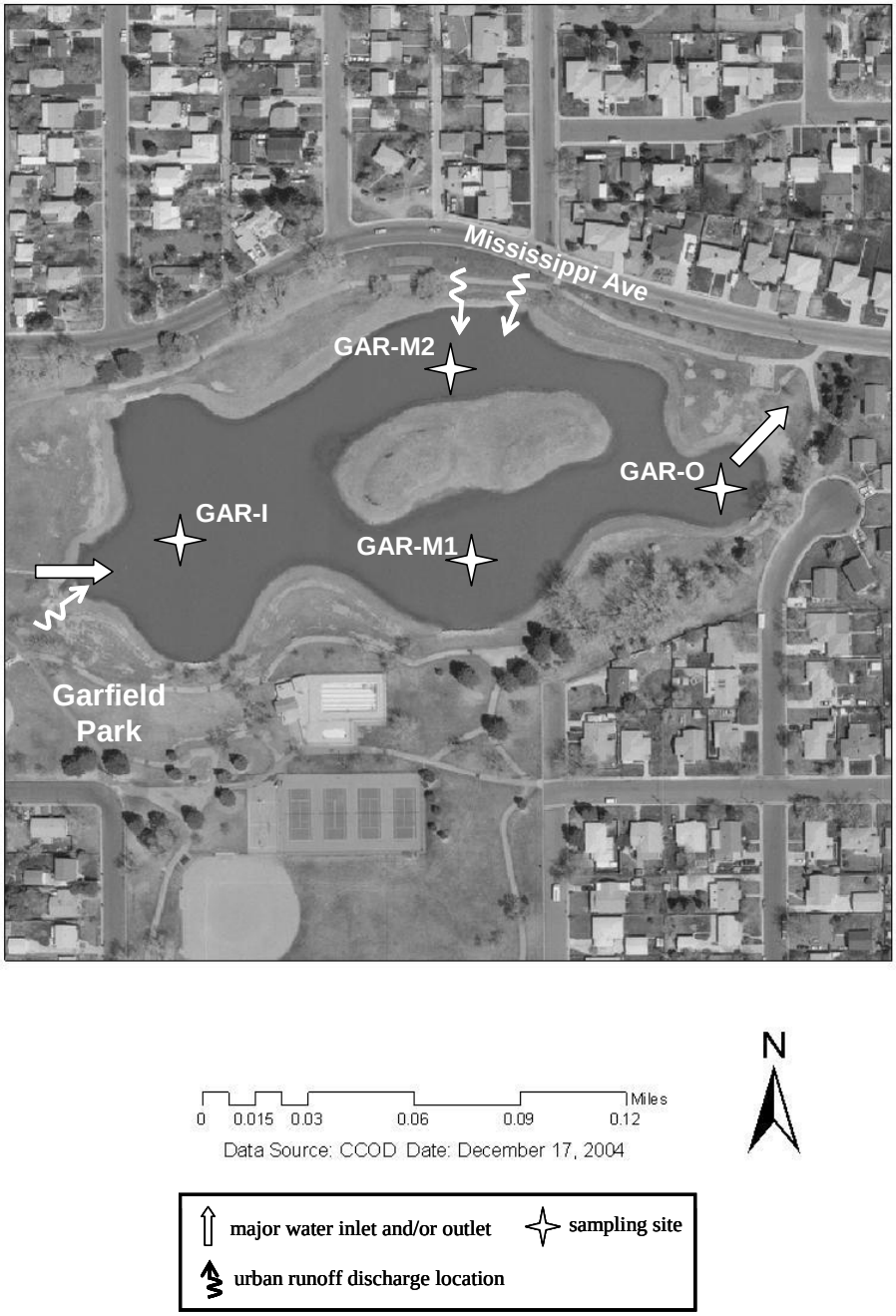


Figure 3-10 Garfield Lake Sampling Locations

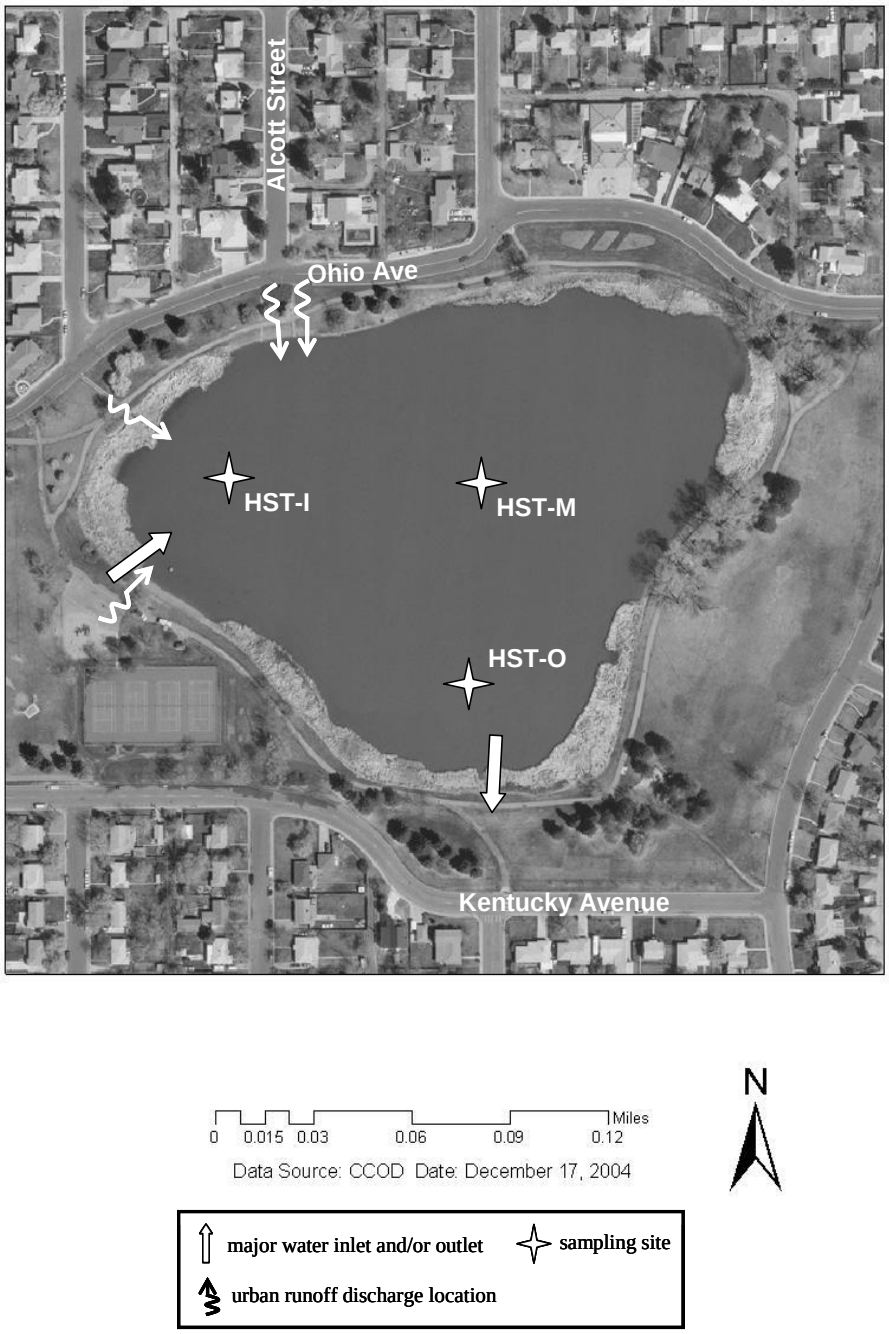


Figure 3-11 Houston Lake Sampling Locations

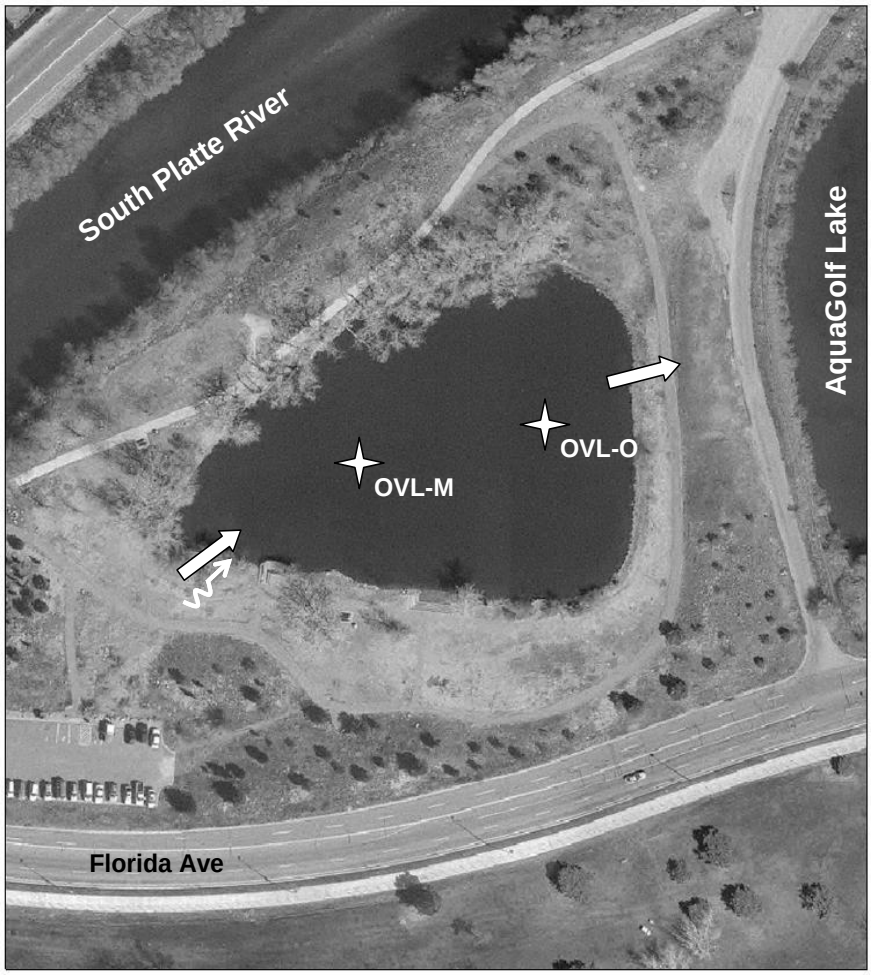


Figure 3-12 Overland Pond Sampling Locations

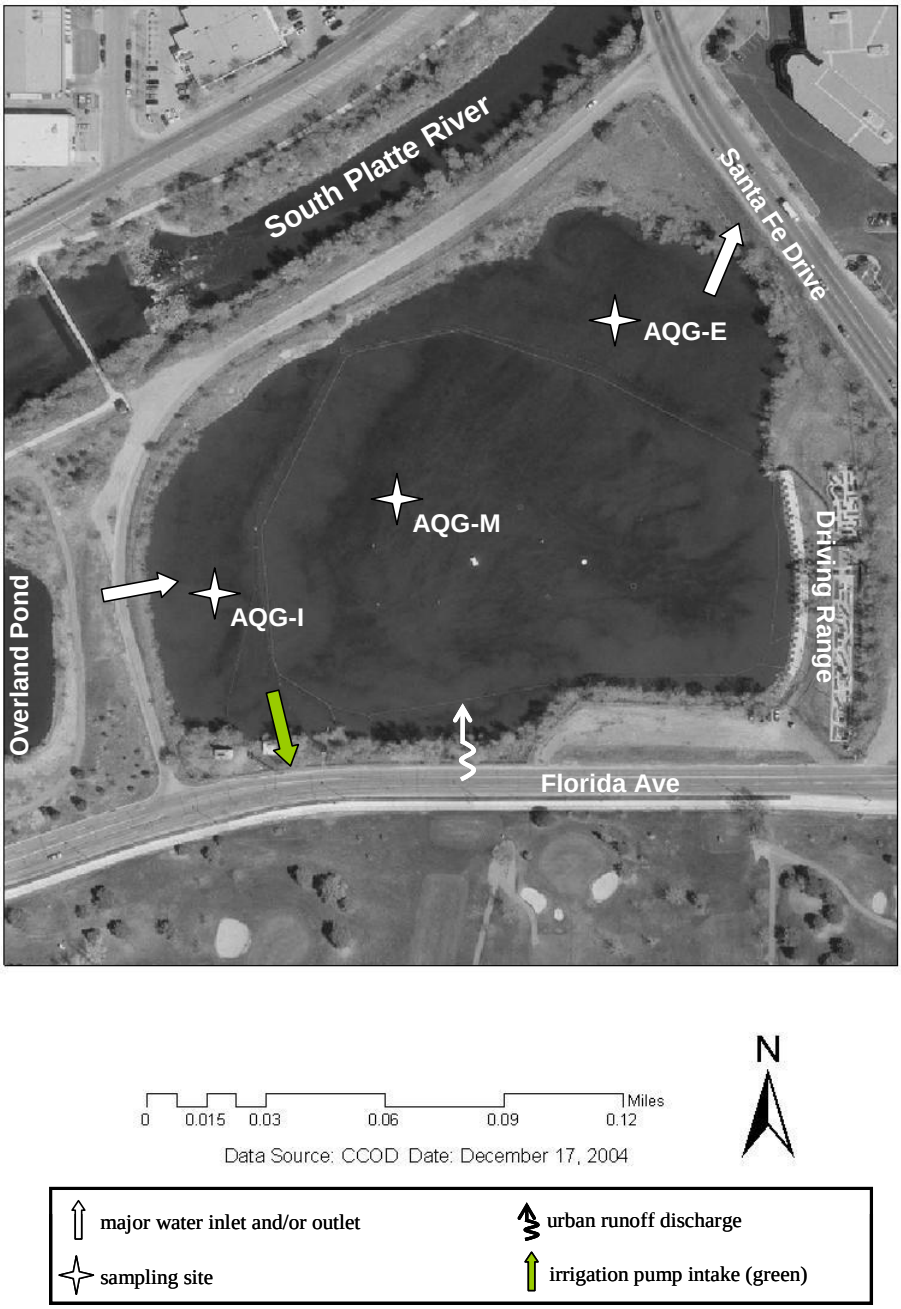


Figure 3-13 Aquagolf Lake Sampling Locations

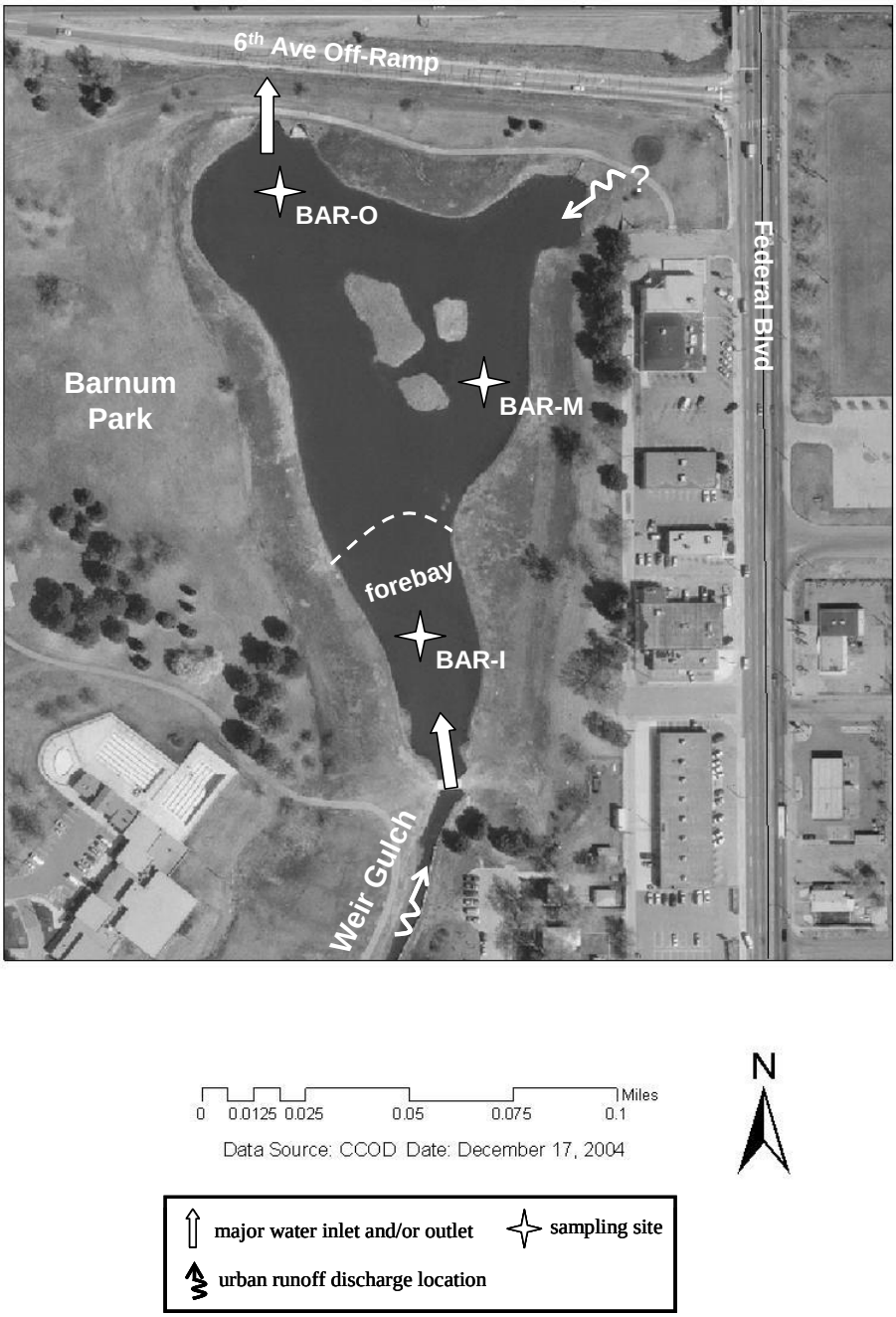


Figure 3-14 Barnum Lake Sampling Locations

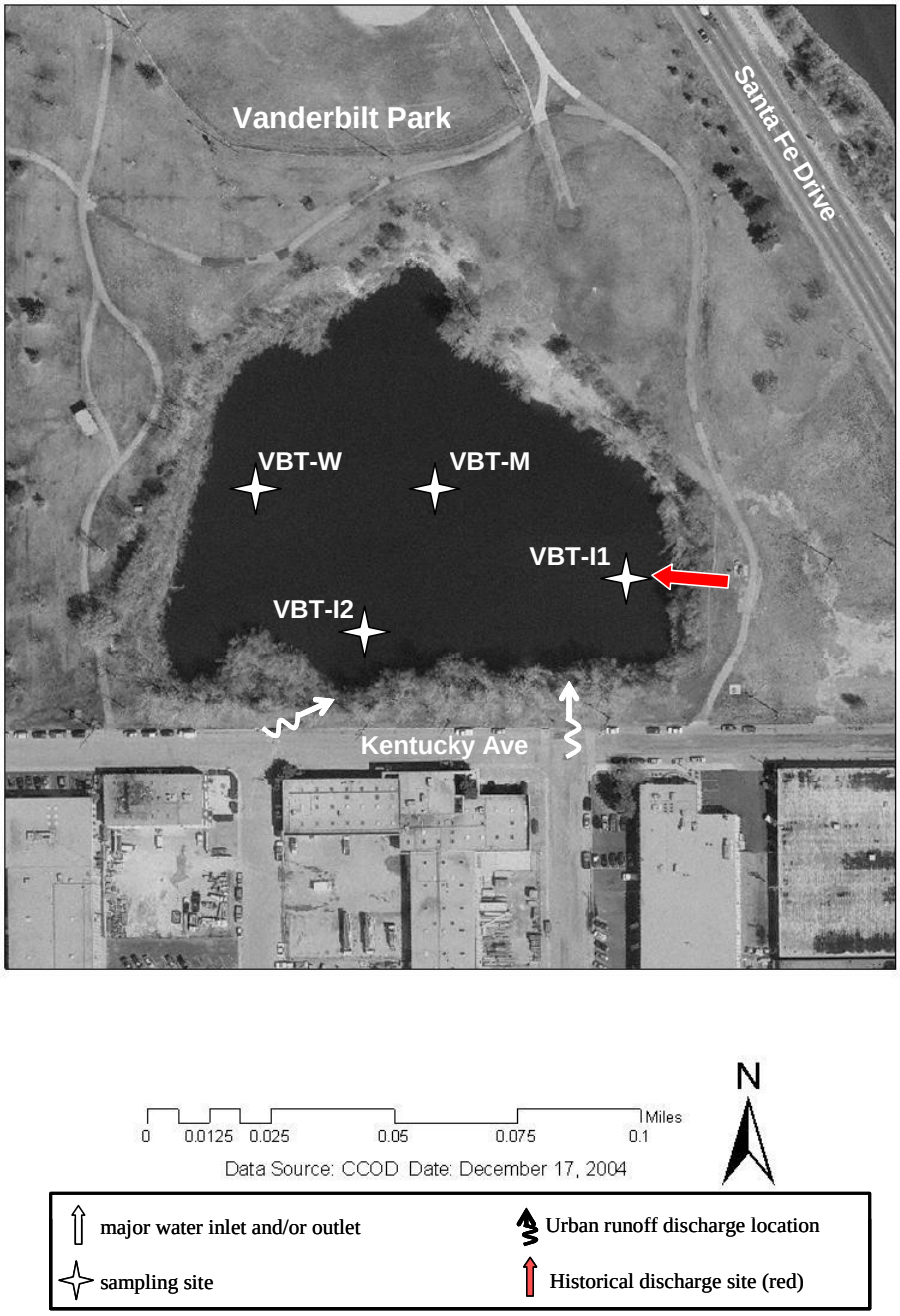
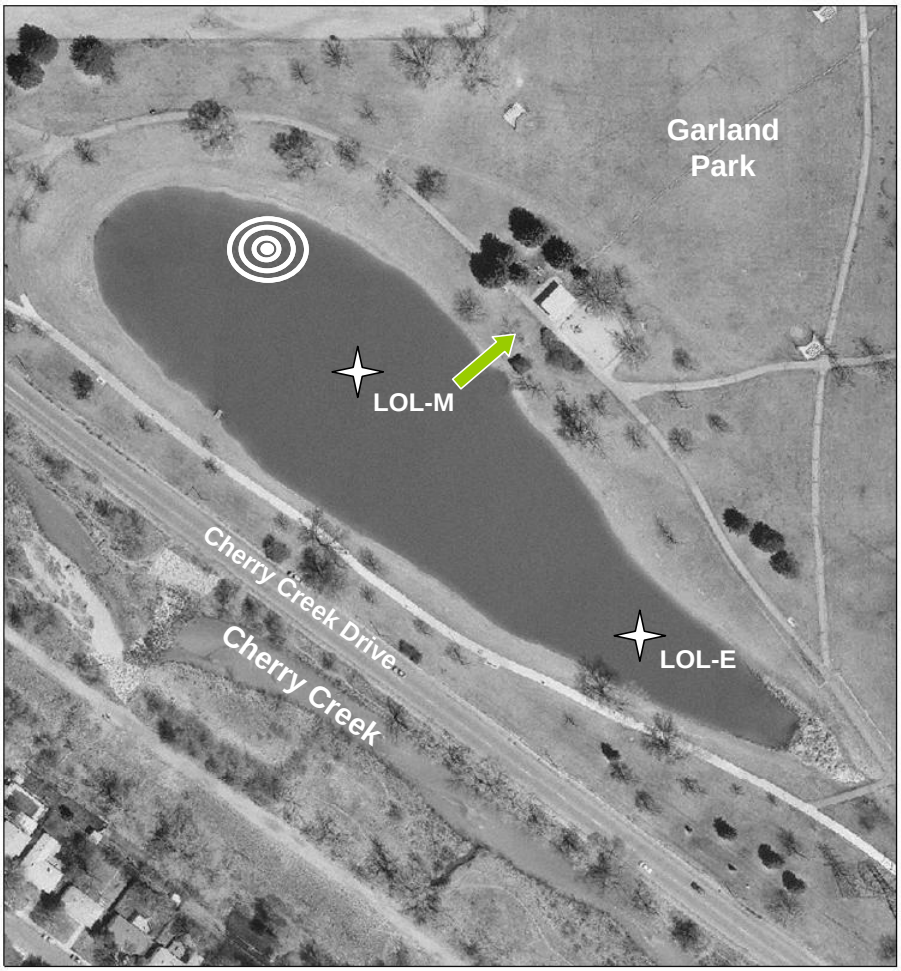


Figure 3-15 Vanderbilt Lake Sampling Locations



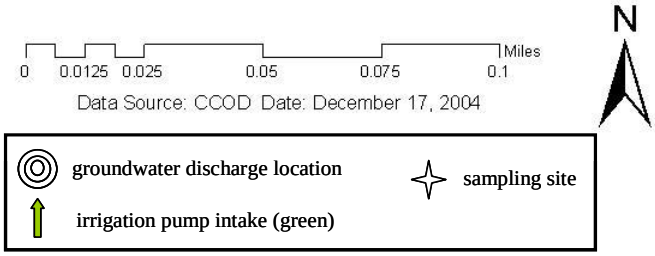


Figure 3-16 Lollipop Lake Sampling Locations

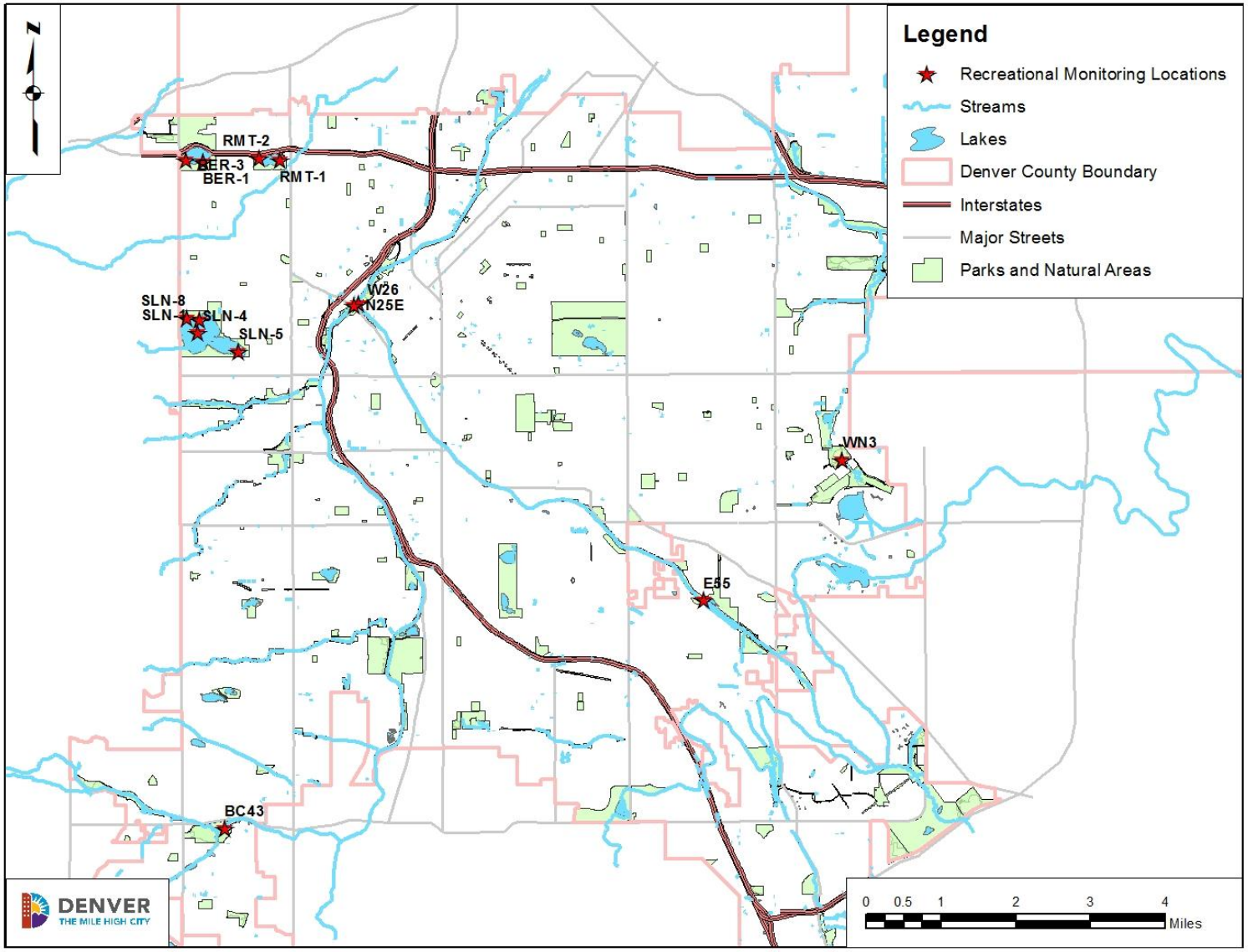


Figure 3-17 High Use Sampling Locations

4.0 Data Validation and Usability

All data generated by the Water Quality Program will be reviewed, verified and validated prior to entry into the Water Quality Program database. The data will also be reviewed to ensure it meets the requirements of the data quality objectives described in Section 2.2.

4.1 Data Review, Verification, and Validation Methods

This Section describes how data generated by the Water Quality Program will be reviewed, verified and validated prior to entry in the watershed database.

4.1.1 Laboratory Data Reduction, Validation, and Reporting

The objective of the Water Quality Program is to provide defensible analytical data that are accurate, precise, comparable between laboratories, representative of the locations of concern, and complete to the degree defined in the data quality objectives. EQD defines data accuracy, precision, comparability, representativeness, and completeness as the following:

Accuracy is a measure of the closeness of sample analysis results to the true value. The accuracy of an analytical method is generally assessed by inserting a series of double blind performance evaluation samples into the laboratory sample stream where the true concentration of the analyte in each double blind sample is known.

Precision is defined as the agreement between a set of replicate measurements without assuming or knowing the true value. Agreement is expressed as either the relative percent difference for replicate measurements or the range and standard deviation for larger numbers of replicates. Data on precision are obtained by analyzing replicate samples.

Data are *comparable* if collection techniques, measurement procedures, methods, and reporting units are equivalent for the samples within a sample set. These criteria allow comparison of data from different sources. Comparable data will be obtained by specifying standard units for physical measurements and standard procedures for sample collection, processing, and analysis. These requirements are specified in SOPs included in Appendix A for sampling procedures and in Table 3-2.

Representativeness is the degree to which data accurately and precisely represent characteristics of a population parameter, variations at a sampling point, or an environmental condition. For this QAPP, Representativeness is ensured by the selection of sampling locations in accordance with the sampling design requirements presented above.

Data are considered *complete* when a prescribed percentage of the total intended measurements and samples are obtained. Analytical completeness is defined as the percentage of valid analytical results requested. For this sampling program, collection of samples at a minimum of 80% of the planned instream or lake sampling locations must be obtained to achieve a satisfactory level of data completeness.

In addition to collection of QA / QC samples to ensure data are defensible (Section 3.5), EQD requires that each laboratory also have a QA / QC program to ensure data are defensible. A summary of EQD's quality objectives for laboratory testing is provided in Table 4-1. The requirements are described in more detail below.

<u>*Internal Laboratory Quality Assurance*</u>
Laboratory duplicate tests (not to be confused with field replicates) will be run on one out of every 20 samples for each medium and analyte. The two results should be within +/- 20% of

each other, if greater than or equal to five times the detection limit or within +/- 100% of the detection limit, if less than five times the detection limit. If outside of these limits, all data associated with the duplicate analysis (i.e., that set of 19 analyses) must be flagged by the laboratory with an "*".

A matrix spike recovery test will be run on one of every 20 samples. Data will be flagged with an "R" by the laboratory if the recovery is outside the range of 75% - 125%, unless the sample concentration exceeds the spike concentration by more than a factor of four. Spike recovery tests are not conducted on field blanks.

Reagent or laboratory control samples will be analyzed at a rate of one for every 20 analyses using EPA quality control solutions or other recognized standards, if available. The percent recovery should be within 80% - 120% of the true value or limits set by the agency supplying the reference samples; if not, the previous 19 analyses will be re-run. Since the control limits must be achieved, there is no flag for being outside of the control limits. EPA (2004b) provides for accepting non-detectable results when the upper control limit is exceeded and otherwise flagging the data as estimated, "J" when the laboratory control samples are outside of control limits.

Internal Laboratory Quality Control
Internal quality control checks will include standard, reference, and calibration blank sample checks for instrument performance; evaluation of laboratory blanks to check for potential sample contamination due to laboratory reagents or deionized water use; and matrix spikes to monitor extraction and recovery procedures. Results of internal quality controls are provided by the laboratory performing the analysis and are to be presented with the sample results in the final report of investigation results.

Performance and System Audits
This QAPP requires that internal quality control samples, blanks, and matrix spikes be analyzed where applicable. All quality control results are reviewed by the analyst daily. In this way, trends in the quality control data are addressed. This continual examination and evaluation of quality control data ensures sample data of high quality.

Field quality control samples will be collected and analyzed to audit field procedures. Results of field quality control analyses are to be presented in the appropriate reports.

Internal Laboratory Data Assessment
Laboratory data will be internally evaluated based upon the criteria presented in the Laboratory QA Manual.

Corrective Action
Corrective Action Taken by the Analyst:

Quality Control Check samples must fall within the specified quality control limits. If the results are outside the limits, sample results are flagged as described above and corrective actions described in the laboratory QA Manuals will be performed.

Duplicate results must agree within 0 – 20% relative difference or sample results are flagged as described above and corrective actions described in the laboratory QA Manuals will be performed.

Matrix Spikes and/or Laboratory spikes and spike duplicates - must agree within 80 – 120% recovery or sample results are flagged as described above and corrective action as described in the laboratory QA Manual will be performed.

4.1.2 EQD Data Review, Validation, and Verification

The following data validation procedures are to be performed before data is entered into the database.

Contract Laboratory
EQD validates results from all samples analyzed by the contract laboratory to ensure that data were produced in accordance with procedures outlined in this QAPP. The data validation process evaluates all individual samples collected and analyzed to determine if results are within acceptable quantitative or qualitative limits for precision, accuracy, representativeness, comparability, and completeness. Each of these terms and the quantitative or qualitative limits of acceptability are discussed in Section 4.1.1. Data validation consists of reviewing the following elements:

- Methodology
- Holding Times
- Sample Preservation
- Calibration
- Blanks
- Spikes
- Replicates
- Duplicates
- Laboratory Control Samples
- Matrix Spike and Matrix Spike Duplicate Samples
- Method Blank Samples
- Laboratory Duplicate Samples

Validation and verification of data packages from the contract laboratory will be done in accordance with EPA's National Functional Guidelines for Inorganic Data Review (EPA, 2004b).

Wastewater Management Laboratory
The City's Wastewater Management Division provides hard copies of analytical results which are reviewed and then manually entered into the water quality database. If review of the data reveals any inconsistencies, the WMD Laboratory is consulted for clarification. If an error or discrepancy is found that cannot be assured to be free of quality concerns, it will be enclosed in brackets (referred to as "flagged"). Data will be evaluated if the origin of the sample is in doubt (i.e., sample numbers appear to be switched from one document to another). Errors will be noted and initialed on the raw data forms, but will not be altered or erased. A single line will be drawn through the error and the correct entry will be written immediately beside the error. After the data has been reviewed, it is entered into the water quality database and is checked against the hard copy to verify data entry accuracy. Any errors are corrected. Once data is entered into the database and verified, the hard copies are filed in the water quality data files.

All samples will be analyzed within the required holding time limits specified in Table 3-2. Samples not appropriately preserved will be invalidated, unless professional judgment dictates that it is more appropriate to flag the data (e.g., consistent with historical observation). Sediment samples require no preservation.

Equipment rinse blank will be collected on an as needed basis for each project using equipment that requires decontamination. All data for events lacking the required number of blanks will be flagged. All data associated with contaminated blanks will be flagged if the blank concentration exceeds 10% of the sample concentration and potentially invalidated if the blank concentration exceeds 50% of the sample concentration (use professional judgment

based on historic concentration and other information). Data will not be flagged if the sampled concentration is below detection, regardless of the blank concentration. Sample results will not be corrected by subtracting the blank concentration.

Field replicates are successive samples and are intended to reflect variations due to sample handling during laboratory analysis. Laboratory influences are also isolated by the analysis of laboratory duplicate samples. Because natural variations in the environment can cause significant variations in concentration, there are no set standards for quality control. Although variations on water samples are generally small, data will not be flagged by the QA Officer unless professional judgment indicated that one or both of the results is questionable based on historic observations or other information. RPD control limits in the range of +/- 50% are general guidelines and may be used for comparison purposes.

4.2 Reconciliation with Data Quality Objectives

All data will be assessed annually to reconcile the data with the DQOs to determine whether the DQOs were attained. If necessary, a report will be prepared to describe how issues were resolved and what the limitations on the use of the data are. The report will also summarize procedures used to define data usability (i.e., data reviews or validation reports) and the results of these procedures.

The review of the usability of data culminates in the determination of whether the collected data set is usable for decisions defined in the DQO process. The review also helps to assess the potential error in the decision. The data usability review begins with an evaluation of the effectiveness of the sampling operations, their conformance to the SOPs, and whether any unusual circumstances are documented in the field logs. The five data quality indicators that will be assessed during the review of field procedures include; accuracy, precision, completeness, representativeness, and comparability (described in Section 4.1). The data assessment criteria for each of these parameters are described in Section 4.1. Generally, data that do not meet the established acceptance criteria are cause for resampling and reanalysis. However, in some cases data that do not meet acceptance criteria are usable with specified limitations, and the limitations must be clearly identified. Indicators of data limitations include data qualifiers, quantitative evaluations, and narrative statements regarding potential bias. An evaluation of the data set determines whether it can provide adequate support for the decision(s) it is meant to support.

Corrective action will be utilized when performance fails to meet objectives for data that is critical to the Water Quality Program. Some corrective actions include the following:

- Retrieving missing information;
- Resolving technical or procedural problems by requesting additional explanation or clarification from the technical team;
- Requesting reanalysis of sample(s) from the remainder stored at the laboratory;
- Requesting construction and re-interpretation of analytical results from the laboratory or team chemist;
- Conducting additional sample collection and analysis for sites in question;
- Adjusting or questioning data based on approved default options and routines; and
- Qualifying or rejecting data for use as part of the Water Quality Program.

Table 4-1 Quality Assurance Objectives; Accuracy, Precision, and Completeness

Parameter	Accuracy (% Recovery)	Precision (% Error)	Completeness
Alkalinity	80 – 120%	0 - 20%	90%
Hardness	80 – 120%	0 - 20%	90%
E. Coli	50 – 150%	0 - 50%	90%
TOC	80 – 120%	0 - 20%	90%
DOC	80 – 120%	0 - 20%	90%
Total Ammonia	80 – 120%	0 - 20%	90%
Nitrite	80 – 120%	0 - 20%	90%
Nitrate	80 – 120%	0 - 20%	90%
TKN	80 – 120%	0 - 20%	90%
Tot. Phosphorous	80 – 120%	0 - 20%	90%
Chloride	80 – 120%	0 - 20%	90%
Sulfate	80 – 120%	0 - 20%	90%
TDS	80 – 120%	0 - 20%	90%
TSS	80 – 120%	0 - 20%	90%
Metals, Dissolved	80 – 120%	0 - 20%	90%
Mercury, Dissolved	80 – 120%	0 - 20%	90%
Metals, Total	80 – 120%	0 - 20%	90%
Mercury, Total	80 – 120%	0 - 20%	90%
VOCs	80 – 120%	0 - 20%	90%
SVOCs	80 – 120%	0 - 20%	90%
Total Organic Halides	80 – 120%	0 - 20%	90%
Gross Alpha / Beta	80 – 120%	0 - 20%	90%
Gamma	80 – 120%	0 - 20%	90%

5.0 Assessment and Oversight

Program assessments are designed to determine whether the QAPP is being implemented as approved. Program assessments provide the assurance that information collected as part of the QAPP may be used for its intended purpose. Assessments should occur as needed both during and after a project has been completed.

5.1 Assessment and Response Actions

Assessments that may be performed as part of EQD's Water Quality Program include, but are not limited to performance audits and technical systems audits. Additional assessments evaluate field meter maintenance and entry of data into the watershed database. Table 5-1 summarizes the components necessary for adequate assessment of the Water Quality Program. It also identifies personnel responsible for the assessments.

5.1.1 Performance Audits

Performance audits are used to determine the status and effectiveness of both field and laboratory measurement systems and to provide a quantitative measure of the quality of data generated. For laboratories, this involves the use of standard reference samples or performance evaluation samples (double blind samples). These samples have known concentrations of constituents that are analyzed as unknowns in the laboratory. Results of the laboratory analyses are compared to the known concentrations of the double blind samples for accuracy and are used to evaluate laboratory performance in relation to the project DQOs. Field performance is evaluated using field blanks, equipment decontamination rinsates (when appropriate), and field replicates. These QC samples are collected by the Field Sampling Team Members.

As the analytical results from the QC samples are received, it is the responsibility of the Field Sampling Team Member to assure that the samples are correctly labeled (QC samples are submitted to the laboratory with false location names which must be corrected prior to entry in the Water Quality Database). This includes correction of the site designation, collection time and date, and field data as well as checking off the appropriate box on the chain of custody section of the field form to indicate the appropriate type of QC sample. The Project Manager must ensure that data from QC samples is immediately reviewed and assessed.

If results require corrective action, the laboratory should be contacted immediately to alert them of EQD's concerns, to initiate an investigation of the results, and to take appropriate actions to remedy the situation.

Prior to completion of a sampling event, an assessment of the QC efforts must guarantee that an adequate number of QC samples have been collected. Adequate time must be allotted prior to this assessment to allow for collection of necessary QC samples before the sampling period is completed.

5.1.2 Technical System Audits

Technical system audits are performed by a third party to confirm the adequacy of the data collection (field operation) and data generation (laboratory operation) systems. On-site audits are conducted to determine whether the QAPP and field and laboratory SOPs are being properly implemented. Technical systems audits are typically only performed if there is a reason to suspect that the adequacy of data collection and generation are not sufficient to meet the needs of the water quality sampling program.

- A systems audit of field procedures assesses and documents at a minimum, sampling methods (including collection, containers, and preservation), equipment decontamination (as needed), chain of custody, sample labeling, QC methodology, equipment maintenance and calibration, and sampling documentation.
- A systems audit of laboratory procedures assesses and documents at a minimum, methods for data qualification, analytical data generation, chain-of-custody documentation and protocol, instrument calibration and maintenance, data reporting, QC methods and QC criteria, and nonconformance corrective action procedures.

Checklists for technical systems audits of field procedures are included in Appendix B.

5.1.3 Other Assessment and Response Actions

Meters
To assure routine maintenance of meters and calibration standards are being performed, a designated person, preferably a member of the Field Sampling Team, should review the meter maintenance logs weekly to bi-weekly. The maintenance logbook for calibration standards will document adequate assessment.

Data
Dynamic database support structure requires that data processing assessments are overseen by the responsible Project Managers. The Project Manager is responsible for assuring that data is properly handled, that it receives an initial review, is validated and entered into the database, that data entry is verified, and that hard copies of the data are appropriately filed. All attempts must be made to expedite the process and assure that data processing does not affect EQD's ability to access and utilize results in a timely manner.

Data processing and database reviews should be performed quarterly for on-going programs and monthly upon completion of seasonal sampling until all results for that sample event have been received and completely processed.

5.1.4 Response to Assessments

Project Managers are responsible for reviewing and taking appropriate response actions to assessment findings. Responses are to be conducted in a timely manner. The response will depend upon the potential impact and / or time-critical nature of the quality problem.

5.2 Reports

Data collected during the field efforts will be reconciled with the project DQOs by preparing summary tables, charts, figures, or performing other types of data analyses that facilitate direct comparison of data collected through the entire extent of the project. Comparisons will be made on a parameter-specific basis, concentrating on the contaminants of concern. Comparisons also will facilitate an analysis of contaminant concentration trends through time and space.

Any necessary documentation and reporting of EQD water quality QA / QC results is incorporated into existing maintenance forms (meter calibration) or annual reports as needed.

Table 5-1 EQD Water Quality Program Assessment Requirements

Subject	Action	Frequency	Perform Assessment	Respond to Findings	Identify / Implement Corrective Actions	Follow-up on Corrective Actions
Sample Logs						
Streams	Sample Calendar Assessment	Monthly	Streams PM	Streams PM	Streams PM	Streams PM
Lakes	Sample Calendar Assessment	Monthly	Lakes PM	Lakes PM	Lakes PM	Lakes PM
Lab & Field QA / QC						
Streams	Assess / Correct QC Site Information	Monthly	Streams PM	Streams PM	Streams PM	Streams PM
	Review QA / QC Data	Variable[1]	Streams PM	Streams PM	Streams PM	Streams PM
Lakes	Assess / Correct QC Site Information	Monthly	Lakes PM	Lakes PM	Lakes PM	Lakes PM
	Review QA / QC Data	Variable[1]	Lakes PM	Lakes PM	Lakes PM	Lakes PM
Meter Calibration / Maintenance				Lakes PM	Lakes PM	Lakes PM
	Assess Meter & Standard Maintenance Activities	Weekly to Bi-weekly[2]	Field Sampling Team Member	Streams PM Lakes PM	Streams PM Lakes PM	Field Sampling Team Member
Data						
Streams	Assess Data Status for Entry, Verification, and Filing	Variable[1]	Streams PM	Streams PM	Streams PM	Streams PM
Lakes	Assess Data Status for Entry, Verification, and Filing	Variable[1]	Lakes PM	Lakes PM	Lakes PM	Lakes PM

Notes:
Table is modified from EPA QA/G-5 (EPA, 2002a).
1 Review data as received, incorporate into annual reports.

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Appendix A
EQD Standard Operating Procedures

List of Procedures

DEH Water Quality Program staff conduct all field activities using the standard operating procedures listed below. For copies of the most recent versions of DEH SOPs, contact the DEH Water Quality Program.

Procedure	Title
LK-001	Sampling Procedures - Lakes
LK-002	Procedure for Using Lake Field Forms
ST-001	Surface Water Sampling Procedures
ST-002	Outfall Sampling Procedures
ST-003	Instream Sediment Sampling Procedures
ST-004	Procedure for Using Field Forms
ST-005	Procedure for Using the Sampling Vehicle Supply Checklist
ST-006	Procedure for Collecting Quality Control Samples
WQ-001	Sampling Procedures – Meter Calibration
WQ-002	Sampling Procedures – Post Sampling Meter Care
WQ-003	Procedure for Field Filtration of Water Samples
WQ-004	Outreach Protocols for High Use Sampling Results
WQ-005	Data Importing Procedures

Appendix B
EQD Forms

List of Forms

DEH Water Quality Program staff use the forms listed in the table below as part of routine sampling operations. For copies of the most recent versions of the forms, contact the DEH Water Quality Program.

Form	Title
FF001	Stream Field Form
FF002	Lake Field Form
FF003	Contract Lab Chain of Custody Form
FF004	Sample Labels
FF005	Meter Calibration – Quality Control Form
MT001	Meter Maintenance Records
QA001	Field Audit Checklist, Stream and Outfall Sampling
QA002	Field Audit Checklist, Lake Sampling

Appendix C
Wastewater Management Laboratory Quality Assurance Summary

Wastewater Management Laboratory Quality Assurance Summary

1.0 Program Description

Introduction

Denver Wastewater Management Division Laboratory generates data from samples provided internally for assessing of Industrial Waste Surcharges to industries within the City and for investigations of possible contamination of the city's storm sewer system. Additional testing is carried out for Denver Environmental Health used in monitoring the overall health of rivers and lakes within the City, and for the Denver Zoo. As such, the Wastewater Management Division Laboratory is the only environmentally oriented laboratory within the city system.

Scope

This manual focuses on the general Quality Assurance (QA) objectives and responsibilities of the Denver Wastewater Management Division Laboratory.

Purpose

The primary purpose of the Laboratory Quality Assurance Plan is to provide guidelines and establish processes by which ongoing laboratory procedures can be controlled, monitored and improved. The existence of guidelines and processes will assure that laboratory procedures are up to date and generate accurate, precise, complete, and defensible data. All data must conform to or exceed federal and state regulations. The intelligent application of methods by the laboratory staff is the foundation of the laboratory Quality Control program.

2.0 Organization and Responsibilities

The Denver Wastewater Management Laboratory functions under the direction of the Director of Operations of the Wastewater Management Division and under the direct supervision of the Quality Control Manager. The analytical staff is comprised of a degreed chemist, a degreed microbiologist, a degreed biologist, a laboratory assistant and an intern.

Other sections, also under the supervision of the Quality Control Manager, supplement the functions of the laboratory as part or of their function:

Quality Control Sampling Section

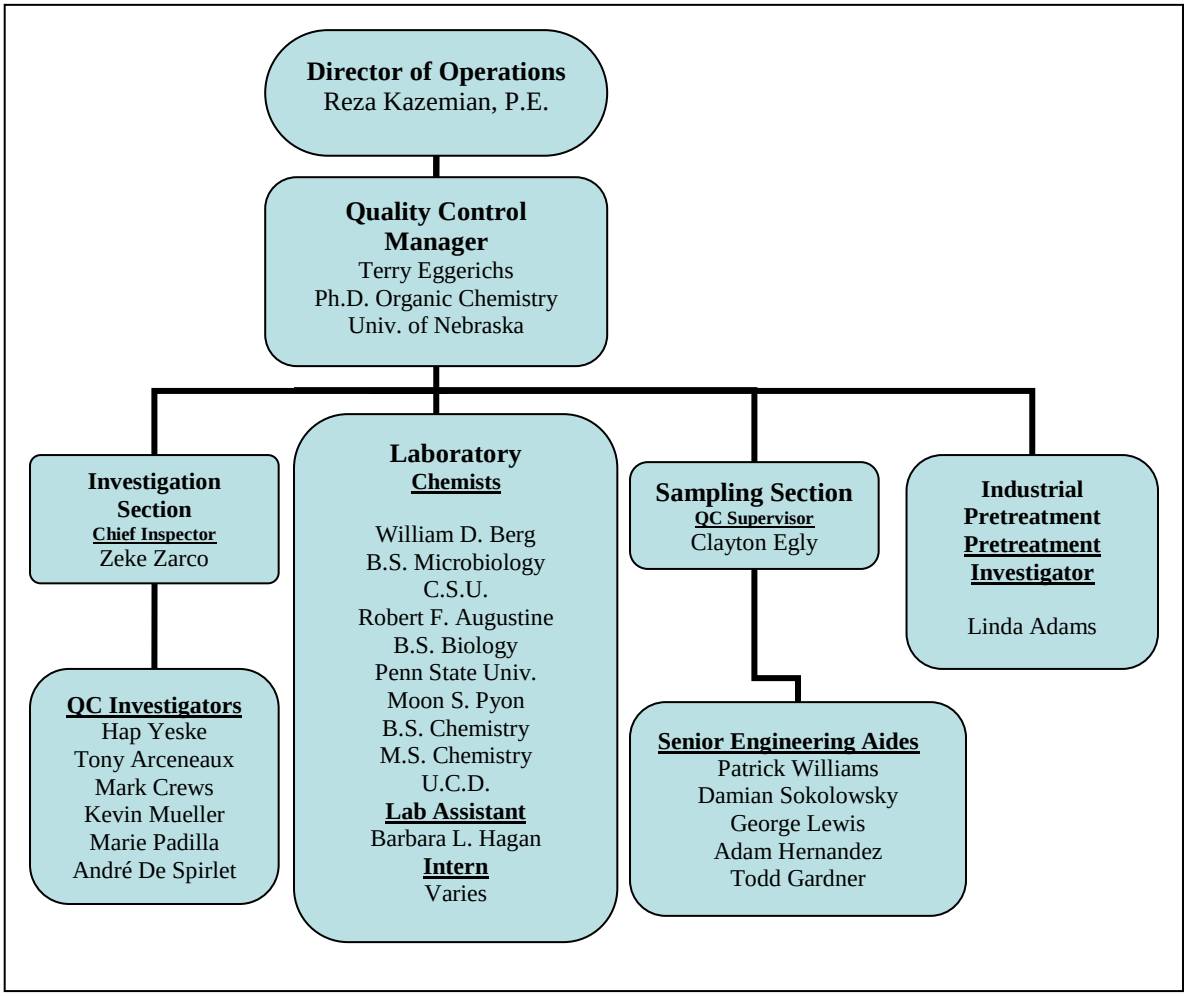
The sampling section functions under the direct supervision of the Quality Control Supervisor. It is comprised of five Senior Engineering Aides who are responsible for flow measurements, environmental sampling of the storm sewers and industrial waste sampling. They also follow up investigations on illicit discharges to the storm sewers originating from broken taps, failed sanitary lines, etc.

Quality Control Investigation Section

The investigation section is comprised of six investigators under the direct supervision of the Chief Inspector. While most of their function is in code enforcement and investigations, they interact with the laboratory by ensuring the repair of disconnected taps impacting the storm sewers.

Quality Control Industrial Pretreatment Section

Industrial pretreatment is handled by one investigator directly supervised by the Quality Control Manager. Although this person deals mainly with the Federal Industrial Pretreatment regulations, she also keeps a data base of industries and businesses in Denver, the information from which is essential in the tracking of unexplained discharges to the storm sewers and for the location of new Industrial Waste Customers.



3.0 Quality Assurance Objectives

Data Quality Objectives

The primary objective of the Wastewater Management Laboratory is to provide those we serve with quality services that conform to valid requirements. To this end, we are committed to producing the highest quality analytical data using standard methodologies.

In order to meet these objectives and to establish the criteria by which the quality of the data generated can be both ascertained and ensured, it is necessary to define certain terms. These terms will aide in describing the laboratory's quality objectives.

Quality Assurance (QA) is defined as the steps taken to confirm that the laboratory QA plan is operating effectively. Quality Assurance includes all the measures in place to produce a product that meets quality objectives.

Quality Control (QC) is defined as a process of confirming that products have met the defined quality requirements.

Precision is the agreement between a set of replicate measurements without assumption of knowledge of the true value. It is a measure of the variability in repeated measurements of the sample compared to the average value. The precision assessment should represent the variability of sampling, sample handling, preservation and storage of the environmental measurement data.

Accuracy is a measure of how close an individual measurement or an average of a number of measurements is to the true value.

Precision and Accuracy for Each Parameter
The Wastewater Management Division Laboratory will meet or exceed the precision and accuracy statements established by ASTM, *Standard Methods for the Examination of Water and Wastewater,* and the US-EPA. Chemists have the responsibility to monitor for non-compliance.

4.0 Sampling Procedures

Introduction

Sampling procedures should ensure the following:

1. Samples should contain no foreign material and accurately represent the site from which the samples are collected

2. Samples must be:

    a. of adequate size

    b. collected in containers appropriate for the sample and the analysis being requested

    c. properly preserved in terms of pH and temperature during transport.

3. Contamination must not occur during transport.

4. When necessary, accurate records are generated and kept regarding site conditions, map of sampling site, labeling of samples, and weather conditions.

5. Monitoring and/or sampling instruments must be working properly.

6. Sampling containers must be properly cleaned.

7. Samples must arrive at the laboratory in a timely manner so as to allow for analysis within the time limitations required of the analysis.

Water Sample Container Preparation

Sampling containers are prepared in a manner consistent with the requirements of the analyte in question, and dependant on the level of analyte concentration and accuracy required by the procedure.

Definitions

A. **Preservative:** A preservative is a chemical compound added to the sample at the time of sampling in order to maintain the target compounds in the same concentration and state as at the time of sampling. Since usually only one preservative may be used per container, more than one container may have to be used when analyzing a wide range of parameters. Many parameters require only chilling with ice to preserve them.

B. **Holding Time:** The holding time is the maximum length of time that can occur between sampling and the actual analysis of the sample. Holding times have been determined by US-EPA for most parameters of environmental significance and are occasionally revised as new data becomes available.

C. **Trip Blank:** A trip blank is a sample container that is filled in the laboratory with matrix material (usually water) that is free of target analytes. Once prepared, it is sealed and sent to the field with the sample containers and will remain unopened during the sampling event. This trip blank sample is used to monitor extraneous contamination that may be picked up during commercial sample shipment and storage. Samples that are hand delivered normally do not require the use of a trip blank.

D. **Field Blank:** The field blank is a sample container that is filled during the sampling process with matrix material (usually water) that is free of target analytes. Depending on the sampling protocol, the field blank may be used to control for both cross-contamination of samples and extraneous sources of contamination (usually from the ambient air).

E. **Container Blank:** A container blank is a sample container this is filled in the laboratory with matrix material (usually water) that is free of target analytes. It is used to control any contamination occurring during the recycling of sample containers or present in new containers.

Water Sample Preservation and Holding Times

Methods of preservation are relatively limited and are intended generally to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce volatility of constituents. Preservation techniques are limited to pH adjustment and control, chemical addition, the use of amber or opaque bottles, refrigeration, filtration, and freezing. Regardless of the sample type, complete and unequivocal preservation is a practical impossibility. The Wastewater Management Division Laboratory utilizes the preservation protocol and holding time requirements established by the US-EPA. A summary of the special handling and preservation techniques is listed below:

Determination	Preservation	Hold Time	Container	Sample
Alkalinity	Cool, 4° C	14 Days	P, G	100 ml
Biological Oxygen Demand	Cool, 4° C	48 Hours	P, G	1000 ml
Bacterial Plate Counts	Cool, 4° C	4 Hours	Sterile P	100 ml
Chemical Oxygen Demand	Cool, 4° C	7 Days	P, G	100 ml

Chloride	None	28 Days	P, G	50 ml
Conductance	Cool, 4° C	28 Days	P, G	500 ml
Hardness	HNO_3 to pH<2	6 Months	P, G	100 ml
Ammonia	H_2SO_4 to pH<2	28 Days	P, G	500 ml
Nitrate + Nitrite	H_2SO_4 to pH<2	28 Days	P, G	50 ml
Nitrate	Cool, 4° C	48 Hours	P, G	50 ml
Nitrite	Cool, 4° C	48 Hours	P, G	50 ml
Dissolved Oxygen	None	8 Hours	P, G	300 ml
pH	None	0 Hours	P, G	50 ml
Total Phosphorous	H_2SO_4 to pH<2	28 Days	P, G	100 ml
Ortho-Phosphate	Cool, 4° C	48 Hours	P, G	100 ml
Sulfate	Cool, 4° C	28 Days	P, G	50 ml
Suspended Solids	Cool, 4° C	7 Days	P, G	200 ml
Dissolved Solids	Cool, 4° C	7 Days	P, G	200 ml
Total Solids	Cool, 4° C	7 Days	P, G	200 ml
Total Organic Carbon	H_2SO_4 to pH<2	7 Days	G	2 x 5 ml
Dissolved Organic Carbon	Cool, 4° C	7 Days	G	2 x 5 ml

5.0 Sample Custody

Introduction:

Sample login is viewed as an important element in laboratory function. Complete and accurate login prevents both the sample and time from being wasted in the analytical process. The following procedures are in place to prevent problems from occurring during the intake and login phase of the analysis.

The chemist assigned to dispensing for the day is responsible for all aspects of the initial sample login. The major responsibility of the dispensing chemist is to assure that accurate sample information is received and documented, enabling a smooth, timely initiation of the analytical process.

Definitions:

Terms commonly used in the intake and login procedures are defined below:

A. Sample Number: The sample number is a number assigned by the customer pertaining to records relevant to the customer.

B. Laboratory Number: The laboratory number is comprised of three sections, each with their own significance. The first section is comprised of two digits and indicates the sample number for samples taken in that day. The next section of the laboratory number contains letters or a two-digit number used to code the source of the sample. The final section indicates the sample number for the year from the customer in question. Thus the laboratory number **35-Z-205** would indicate the sample was the 35th sample that day received in the laboratory. The **Z** indicates that the sample originated from the Denver Zoo. The **205** indicates that the sample was the 205th received for the year from the Denver Zoo.

C. Chain of Custody is a legal document indicating the transferal of the current possession of a sample or group of samples. In addition, the document usually conveys information concerning sampling and analytical requests.

Sample Intake and Login:

The samples and associated paperwork are delivered to the sample intake area, where the chemist assigned to dispensing takes custody of them. The samples are recorded in the laboratory log and given a laboratory number which is also recorded on the chain of custody form and the sample container.

The samples are retained at the dispensing area where the chemists assigned to various tests dispense portions of the sample to be used in their assigned tests. Each aliquot is labeled with the laboratory number. Any analysis with a short holding time is given priority over analyses with longer holding times. All portions of the sample are stored with refrigeration if not immediately analyzed.

6.0 Calibration/Standardization Procedures

Introduction

This section defines calibration and standardization procedures and their frequencies when performing analytical testing by instrumental or classical chemistry techniques.

Instrument Calibration and Frequency

Before valid data can be obtained from any instrument, it must be properly calibrated. Calibration must be planned in such a way as to establish detection limits and to determine the range of linear response of the instrument. Data will not be accepted that requires extrapolation out of the established linear range. Initial, operational, and periodic calibration will be performed according to the guidelines of the manufacturer, the requirements of the analytical method, and/or special requirements of those submitting the sample.

Chemistry Methods – Standardization and Frequency

As in instrument calibration above, calibration and standardization procedures of chemistry methods must also be performed to ensure the analytical system is functioning correctly before analyzing samples. Most wet chemistry methods today require some sort of instrumentation in the procedure, i.e. spectrophotometer, pH meter, auto-analyzer, etc. It is imperative that all instruments are calibrated according to the guidelines of the manufacturer, the requirements of the analytical method, and/or the special requirements of those submitting the sample.

7.0 Analytical Procedures

Analytical Methods:

A large amount of the analytical work performed by the WMD Laboratory is completed to support the regulatory requirements of the Clean Water Act. Under the Clean Water Act (CWA) any organization that discharges wastewater into any river system is subject to regulation under the National Pollution Discharge Elimination System (NPDES). Various methods are approved or mandated by this act. Environmental samples analyzed under the CWA shall be analyzed in accordance with EPA approved methods listed in the Federal Register 40 CFR Part 136 or in future rules promulgated by EPA to designate methods approved by the administrator as required by the CWA. These methods are detailed in the latest edition of *Standard Methods for the Examination of Water and Wastewater.*

It is the obligation of all chemists in the WMD laboratory to see that these methods are not compromised.

8.0 Method Detection Limits

Introduction

The purpose of this section is to define the minimum steps to be taken which will demonstrate the laboratory's capability to perform a given analytical method. For methods utilized by the laboratory, a method detection limit study will be performed that follows the procedure as published in the *Code of Federal Regulations;* Title 40, part 136, appendix B, revision 1.11, 1992. This method detection limit study is used to demonstrate that the method being evaluated:

A. actually measures the parameter it proposes to measure,
B. accurately quantifies the parameter, and
C. has known limits of precision and detection.

The results of these studies, which will take the form of a series of precision and accuracy statements, will be maintained by the laboratory staff and will be made available upon request.

Detection Limits – General Information

The above procedure defines the minimum effort required to establish an analyst's capability to perform an analytical method, but the analyst should also be aware of other terms often used within the industry and relate these terms to their application.

Instruments have an inherent sensitivity in the detection of analytes. This sensitivity is expressed in terms of detection limits and will vary from one instrument to another, from one method to another and from one analyte to another. It is necessary to establish those limits before using an instrument and to monitor them on an ongoing basis during analysis. The SOP for an instrument must define the means by which detection limits are established.

The following are definitions of some commonly used terms:

IDL – Instrument Detection Limit – is the minimum signal strength above background an instrument can detect at a specified confidence level. It is measured by analyzing replicate blank samples.

MDL – Method Detection Limit – is the minimum signal strength necessary to qualitatively identify an analyte by a specific protocol at an appropriate confidence level. The MDL is measured by analyzing a set of solutions having a range of known concentrations of the analyte in question. Those concentrations should begin at the expected MDL for the instrument, method, and analyte. The range will be method dependent. It is calculated by the standard deviation times the Student t-value at the desired confidence level.

LOQ – Limit of Quantitation – is the minimum signal strength necessary to determine the concentration of the analyte by a specific procedure at the desired confidence level. It is measured by analyzing a minimum of seven replicates spiked at concentrations ranging from one to five times the expected MDL. It is calculated at ten times the standard deviation of the MDL.

PQL – Practical Quantitation Limit – is the lowest level that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions.

Wastewater Management Division Laboratory MDL and LOQ values are listed below for tests commonly used in environmental monitoring. Methods listed are from *"Standard Methods for the Examination of Water and Wastewater*, (21st Edition). Cross references to US-E.P.A. method numbers can be found in the procedural sections of this reference with precision and bias data for the method.

Analyte	**Method**	**MDL (mg/l)**	**LOQ (mg/l)**
Alkalinity	SM 2320 B	5	10
Hardness	SM 2340 C	2	6
E. Coli	SM 9222 D	10	10
F. Coli	SM 9222 D	10	10
T.O.C	SM 5310 C	1.0	2 – 5
D.O.C	SM 5310 C	1.0	2 – 5
Total Ammonia	SM 4500 NH_3 H	0.01	0.1
Nitrite	SM 4500 NO_2^- B	0.008	0.01
Nitrate	SM 4500 NO_3^- I	0.01	0.2
TKN	SM 4500 N_{org}	0.50	1.0
Total Phosphorous	SM 4500 P B5 +H	0.006	0.08
Ortho Phosphate	SM 4500 P B	0.006	0.08
Chloride	SM 4500 Cl^- G	0.15	6
Sulfate	SM 4500 SO_4^{-2} G	7.2	50
TDS	SM 2540 C		10
TSS	SM 2540 D		4

9.0 Data Reduction, Validation, and Reporting

Introduction

The purpose of this section is to detail the steps to be taken in preparing and validating data for final release and to assign responsibility for problem resolution.

Confidentiality of Data

All data generated for the accessing of Industrial Waste Surcharges is held in the strictest confidence. The data is not subject to release under the Federal Freedom of Information Act because city government agencies are exempted from the requirements of this Act. It is further exempted from release under the Colorado Open Records Statutes because the data relates to financial records of the company in question, which are exempted from release by these statutes. Relevant to the above, the following rules are to be strictly adhered to:

1. Data in any form is to be reported only to the company whose name appears on the report sheet, or their assigns.

2. Primary analytical data should never be removed from the laboratory without the specific approval of the Quality Control Manager.

3. Details of any analysis should never be discussed with anyone outside the laboratory without the specific approval of an operations' official of the company in question.

A. Analytical Request Validation: In order for the data generated to be usable, certain methods and procedures must be followed. While that aspect of reporting is covered in other sections of this plan, it is summarized again below. Note that the chemists are asked to assume much of the responsibility for this aspect of validation because they are required to have an intimate knowledge of all tests, methods, and procedures.

1. The sample must be appropriate to the analysis requested. It is the responsibility of the dispensing chemist to apprise the person submitting the sample of any problems relating to such things as insufficient sample, wrong preservative, or problems of a similar nature.

2. It is, further, the responsibility of the dispensing chemist to ensure that the analyses requested have been outlined on the chain of custody form.

3. It is the responsibility of the chemist assigned any given test to monitor the holding time and assure the time is not exceeded. Any violated holding times are to be noted as such on the final report.

4. In the absence of specific instructions from those submitting the sample, it is the responsibility of the chemist assigned any test to ensure that analytical methods and procedures used are appropriate to the request received.

B. Analytical Record Keeping: During the login process, chain of custody forms, containing the requested analyses, are received for each sample. Copies of these sheets, when completed, become part of the sample data package retained. The following steps must be taken in the completion of these sheets:

1. As each chemist completes the analysis for a specific parameter or group of parameters, it is his or her responsibility to ensure that:

    a. The results are correctly transcribed into the analytical notebook or instrument print out. These documents must contain the date of the analysis, reporting units, and the chemist's initials. In the case where holding times are low, the chemist should also record the time the test is initiated and the time the test is completed. This mainly applies to tests such as bacterial plate counts.

    b. The results are then transcribed to the chain of custody form and initialed by the chemist performing the test

    c. The dispensing chemist certifies that all analyses are complete.

    d. The chain of custody forms, with the analytical data recorded, are copied and retained in hard copy, organized by laboratory number for each given sample source.

2. Prior to release of data to the customer, the chemist assigned to each analysis reviews for internal consistency and reasonableness, all calculations

are checked for error, verification is made on all QC data, and only then is the analysis document released.

3. It is the responsibility of the data entry staff to correctly enter all data from the hard copies to the computer files maintained for each sample source.

10.0 Numerical Data and Calculations

Introduction:

The purpose of this section is to define a number of concepts used in the calculation and reporting of numerical data. This will serve to standardize calculation and reporting procedures so that consistent data can be reported.

Method Detection Limit:

Unless otherwise specified in a specific QC protocol or method, the laboratory uses the US-EPA definition of Method Detection Limit (MDL) as stated in 40 CFR pt 136, App. B. pg. 569 (7/1/93 ed.):

"The method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing an analyte".

Refer to the Method Detection Limit section of this plan for information of how this MDL is calculated. This definition is applied to all results that are reported for regulatory purposes and, in most cases, the MDL is listed in the promulgated method. Many other definitions of MDL exist and are usually operationally defined. In method development or experimental work, the analyst may select a more appropriate definition but the basis of the MDL must be stated in the analyst's notes. In all cases it is the responsibility of the chemist running the test to assure that the reported MDL for any analyte is achievable. It is the practice of the laboratory to report as "<" all target parameters whose concentration calculates to less that the MDL. Target parameters whose concentration equals the MDL are reported. Unless a method specifies "zeroing" measurements to a blank, the concentration of target parameters found in a blank are not subtracted from the final results.

Significant Figures:

The determination of significant figures in a number is a simple concept that is covered in most introductory scientific textbooks. The application of these simple rules can, however, present rather perplexing problems when applied to the calculation and reporting of analytical results. The rules used by the Wastewater Management Laboratory are summarized below:

A. All non-zero digits in a number are significant. (125.8 has four significant figures).

B. All zeros appearing between non-zero digits are significant. (10.01 has four significant figures).

C. All zeros appearing to the right of the last non-zero digit in the mantissa are significant. (1.370 has four significant figures).

D. If only zeros appear in the mantissa, then all zeros are significant. (1.000 has four significant figures).

E. All zeros which function only as place holders are not significant. (27000 has only two significant figures).

F. To eliminate ambiguity, the following conventions should be used in writing and reporting numbers:

1. If a number consists only of a decimal portion, a zero should always represent the integer portion. (.0091 should be written as 0.0091: Note that the number still contains only two significant figures).

2. Considering rule E above, there are occasions when the place holders in this example may, in fact, be significant. Taking the example in E, the number 27000 might represent a measurement to be reported at five significant figures. If this is the case, the number should be reported with a decimal point after the integer portion to indicate that the three zeros are significant: (27000.) An alternate way of handling ambiguity in this example is to eliminate the place holders in the case where two significant figures are indicated. In this case, 27000 ug/l could be reported as 27 mg/l. This latter method is frequently not usable since reporting requirements often dictate the units to be used.

G. In preparing the final report, the precision of each measurement making up the calculation of the final result for a specific parameter must be considered. This usually involves rounding the final result to the precision of the most imprecise measurement used in the calculation. Note that the rounding off should be carried out as the final step. The following guidelines should be used for reporting of data:

1. For direct-read instruments, such as pH, results are reported at the instrument limit. (3 or 4 significant figures for pH).

2. In methods where analytical weight measurements of less than a gram is the limiting factor, a maximum of four significant figures will be reported.

3. In methods where a volumetric measurement is the limiting factor, a minimum of two significant figures will be reported.

Rounding Off:

To insure laboratory consistency, the following rules, except where dictated by a specific protocol, shall be used in rounding off data:

A. If the digit beyond the last figure to be kept is less than five, then the figure to be kept remains unchanged. (6.34 rounds to 6.3).

B. If the digit beyond the last figure to be kept is greater than five, then the figure to be kept is increased by one. (6.36 rounds to 6.4).

C. If the digit beyond the last figure to be kept is five and there are no other digits, or if the digits beyond the five are all zeros, then the last figure to be kept:

   1. Remains unchanged if it is even.

   2. Is increased by one if it is odd. (6.35 rounds to 6.4, 6.3500 rounds to 6.4, and 6.45 rounds to 6.4).

D. If the digit beyond the last figure to be kept is five and there are any non-zero digits beyond five, then the figure to be kept is increased by one. (6.l4501 rounds to 6.5).

E. Only one rounding operation should be performed per result. Successive rounding should not be performed. (6.346 rounds to 6.3). Using successive rounding would cause it to be rounded first to 6.35 and then to 6.4.

Statistical Data:

Data may be used to perform certain statistical calculations. It is both permissible and helpful to estimate significant figures beyond what would normally be reported. The following describes several uses of the data and indicates how the calculations are performed:

A. **Mean:** The arithmetic average of a set of data. It is calculated as the sum of all results divided by the number of results. On a calculator with statistical functions, this is the x (X bar) function key. Means should be reported as one significant figure more than the data used to calculate them. In a normal distribution of results, the mean is an indicator of the mid-point of the distribution.

B. **Standard Deviation:** Standard deviation is the root-mean-square deviation of results from the mean. It is calculated as the square root of the sum of the squares of the differences (result-mean) divided by the number of results. On a calculator with statistical functions, this is the on (sigma n) or the on-1 (sigma n-1) key. For a set of results whose number is less than 30, the non-1 key is used. In a normal distribution of results, the standard deviation is a measure of the amount of dispersion from the mean and can be used to help determine the probability that a certain result lies within a specific distribution. Standard deviation should be reported with the same number of significant figures as the mean for the same set of data.

C. **Percent Relative Standard Deviation:** Percent relative standard deviation (%RSD) is calculated by dividing the standard deviation of a distribution by its mean and multiplying by 100. The %RSD presents a quick way to look at the extent of dispersion within a distribution. It is frequently used to evaluate calibration data since a high value for a distribution of response factors would indicate a lack of linearity.

D. **Coefficient of Variation:** The coefficient of variation is calculated in an identical manner as RSD, but is more commonly used to determine if replicate analyses on a given sample repeat within a given confidence level. The value

can be used to reject one or more of several values which deviate most from the mean to reach a given value of CV.

E. **Duplicate:** Duplicate measurements are two independent measurements of the same parameter in the same sample. Duplicates must be comprised of identical quantities of analyte(s) in an identical matrix. Thus, preparation of duplicate samples must arise from the same, properly split container. Relative Percent difference (RPD) is used as the control value for duplicates. RPD is calculated as the absolute difference between the duplicate measurements divided by the mean of the duplicate measurements times 100. The RPD provides an indication of the precision (reproducibility) of the measurement (as the RPD approaches zero, precision increases). RPD should be reported with one significant figure more than the results used in the calculation. For samples that are analyzed in duplicate, the average of the two results is reported.

F. **Spike Recovery:** A sample (matrix spike) or blank (reference spike) with a known amount of target parameter (analyte) added is analyzed. Any background in the sample or blank is subtracted from the spike measurement. Background refers to the concentration of the analyte already in the sample before spiking. The percent spike recovery (PSR) is calculated by dividing the final result by the amount added and multiplying by 100. The PSR provides an indication of the accuracy of the measurement (as the PSR approaches 100, from either direction, accuracy increases). The spiking material should be either a standard reference material or a standard that has an origin independent of that used in the test's standards used for calibrating the method.

G. **Spike/Spike Duplicate:** Two portions of a sample are spiked and analyzed. This procedure is a combination of D and E above and has the advantage of producing both accuracy and precision data. This procedure is particularly useful when the target parameter is not present in the sample and the usual duplicate data would therefore give no indication of precision.

H. **Precision:** As defined earlier, precision is a measure of how reproducible a measurement is. That is, if the same quantity is measured a number of times, how closely are the data values grouped. Standard deviation is the most commonly used measure of precision. Standard deviation is calculated using the equation below, where s is the standard deviation of a quantity X measured n times where n < 16.

$$s_{N-1} = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \overline{x})^2}\ .$$

The larger the standard deviation, the more imprecise the measurements. If an error in data collection is truly random, 68.3% of the measurements will fall within plus or minus one standard deviation of the mean and 95.5% will fall plus or minus within two standard deviations of the mean. There is one difficulty that arises: When doing chemical analyses on environmental samples, it is not usually feasible to evaluate the larger number of samples necessary to use standard deviation or even "student" t-factor as a measurement of precision. Generally as noted, sample duplicates are used to determine the precision of an analysis. The measured precision used for analysis is relative percent difference (RPD) where D1 is the sample value and D2 is the sample duplicate value:

$$\text{RPD} = \frac{(D1 - D2)}{(D1 + D2)/2}(100)$$

When RPD's have been determined for enough samples (i.e., 10 or more), the average RPD and the standard deviation of the RPD can be calculated. Control charts to detect out of control trends can be constructed from these data. The limit of acceptability is usually set at plus or minus two standard deviations.

I. **Accuracy:** Accuracy, in general, is a measure of how close a measured value is to a true value. Unfortunately, for field samples, the true value is unknown. It is, in fact, the quantity that ideally will be established. It is possible, however, to measure the accuracy of measurements using matrix spikes. The recovery of spiked analytes is monitored and used to calculate percent recovery as a measure of the accuracy of the measuring system. The percent recovery (%R) is calculated by the formula below where SSR is the analytically determined spiked sample concentration, SR is the analytically determined sample concentration, and SA is the true concentration of the spike.

$$\%R = \frac{(SSR - SR)}{SA}(100)$$

The true concentration of the spike (SA) is calculated as follows.

$$SA = \frac{(\text{Spike concentration in mg/l})\ (\text{Volume in ml of spike})}{(\text{Volume of sample in ml} + \text{Volume of spike in ml})}$$

When %R's have been determined for enough samples (10 or more), the mean percent recovery and standard deviation of percent recovery can be calculated and used to create control charts for evaluation of out-of-control trends in accuracy. Control limits are usually set the same as in control of precision as plus or minus two values of standard deviation.

11.0 <u>Internal Quality Control Checks</u>

Introduction:

This section defines the Wastewater Management Division Laboratory's quality control procedures that are to be used. These procedures define the requirements for the generation of quality control data and the subsequent evaluation of this data. To summarize these procedures, the individual analysts are responsible for performing all relevant quality control procedures and measurements and assuring that the appropriate documentation is completed and readily available for inspection. The analyst also has the responsibility for performing the initial evaluation of the quality control data to determine acceptance with respect to established criteria.

General Quality Control Policies

As stated above, it is the responsibility of each chemist to perform all necessary quality control procedures/measurements and complete all appropriate documentation. Many of these requirements are specified in the methodologies and are addressed in specific method SOP's. There are, however, several quality control policies which are applicable to the majority of analytical procedures. They are as follows:

1. Prior to the analysis of any sample, the analytical system must meet the required calibration criteria. The calibration should then be verified by analyzing an independent standard. All calibration information must be appropriately documented and retained for future reference.

2. Prior to any sample analysis, a method blank analysis will be performed to demonstrate that the analytical system is void of contamination.

3. Associated with any sample "batch", a minimum of 10% quality control measurements must be performed. This 10% may include any combination of duplicate analyses and spike analyses or a spike/spike duplicate analysis. Small sample batches must include a minimum of one duplicate analysis, one spike analysis, and one QC sample analysis.

4. Any quality control measurement which exceeds the established acceptance criteria must be evaluated before additional samples are processed.

Corrective Steps:

As previously stated, it must be demonstrated that the analytical system is in calibration and void of contamination prior to sample analysis. When QC measurements fall outside of the established acceptance criteria, the analytical system is said to be out of control. Once an out of control situation has been identified, sample analysis will stop and the following corrective steps will be followed to define the problem. These corrective steps will not be applicable to every out of control situation. When these steps can not be followed, the chemist will take alternative measures to define the analytical problem.

A. The initial corrective step is to verify all calculations including pertinent calibration calculations and analytical standard preparation.

B. If all calculations are confirmed, reanalyze the QC sample. If the reanalysis results are in control, corrective steps end. If the results reproduce but are still out of control, further investigation is necessary. This situation could indicate a sample preparation error, an instrument problem, or a matrix problem.

C. Analyze a known reference material (check sample) to determine if the analytical system is in control. If the check sample analysis is in control, this indicates that the instrument is in control and that the problem could be a sample preparation problem or a matrix problem. If the check sample analysis is not in control, then the analytical system is said to be out of control and all data generated from the previous sample batch is invalidated. Prior to sample reanalysis, all necessary steps will be taken to bring the analytical system back into control. This could require instrument maintenance or instrument re-calibration.

D. Analyze a second QC sample aliquot. In addition to this aliquot, prepare a check standard and a second QC sample in a similar matrix. Carry all three samples through the entire analytical process concurrently. The check sample analysis serves to monitor the sample preparation procedures during reanalysis. If the check standard analysis is acceptable, then the QC sample analyses are evaluated as follows:

1. If the reanalysis of the original QC measurement is still out of control but the second QC measurement is in control, a matrix problem has been identified and corrective steps end. Document all corrective steps.

2. If both QC measurements are in control, then the out of control measurement probably resulted from a sample preparation error and all data for samples prepared with the QC sample are suspect.

As indicated above, these corrective steps will not be applicable to every out of control situation. Special procedures are to be followed when evaluating QC such as QC measurements acquired from analyses performed using an auto-sampler.

Auto-sampler Data: Because data acquired by using an auto-sampler is not typically evaluated until the sample sequence is complete, special procedures must be utilized to monitor the analytical system during the sequence. This monitoring process involves bracketing sample subgroups with check samples. When the data is evaluated, the check sample results are confirmed. Data falling between two confirmed check samples is accepted if all other QC measurements are in control.

Control Charts

The control chart is a alternative means of presenting the QC data and for looking at trends in the data. By having available a current control chart or data print-out for the method in question, the analyst can make quick calculations of the current QC data to help judge the status of the analysis. As time permits, the control charts can be updated. The essential features of the control chart are:

A. The chart allows the analyst to determine which data points (representing QC measurement events) are part of an out-of-control population and therefore indicative of possible problems in the analytical system. This procedure allows the analyst to empirically differentiate between normal variation inherent in any measurement process and that variation attributable to a process moving away from the normal.

B. The chart is particularly useful for uncovering "trending". Trending is the characteristic of data in a given population to cluster on one side of the mean or to show greater separation from the mean when the population changes. Such behavior indicates to the analyst that the measurement conditions may also be changing and investigation of the system may be warranted. This type of information is best uncovered by the control chart and frequently provides empirical support for an analyst's intuition about the condition of an analytical system.

Axes: The axes of a general control chart are as follows:

A. The X axis is time, which each segment representing a specific sample analyzed on a specific date. The latest being the furthest from the origin.

B. The Y axis is in the units of the control measure being made.

Types of Control Charts: The following types of control charts may be generated to provide feedback to the analytical staff:

A. **Duplicate Control Charts:** A relative percent difference (RPD) is calculated from duplicate measurements. A mean RPD is calculated from the duplicate analyses of the specified population and this mean is used as the basis for control limits.

B. **Spike Control Charts:** A percent spike recovery (PSR) is calculate from spike measurements. A mean PSR is calculated from the spike analyses of the specified population and this mean.

C. **Spike Duplicate Control Charts:** A mean RPD is calculated from the matrix spike/matrix spike duplicate analyses.

Mean (X) Line: The mean line is the value of the mean of the control measurements extended across the graph parallel to the X axis. The degree of deviation from this line is used to determine the control state of any measurement. In establishing data for new methods, the mean line is allowed to "float" until a sufficient number of measurements are made (30 or more).

Control Limit Lines: The control limits are a function of the standard deviation of the control measurements. These are usually represented as lines drawn parallel to the X axis and placed at X plus or minus ko: where k is a constant derived from various probability functions and o is the standard deviation. The x plus ko line is called the upper control limit (UCL) and the x minus ko line is the lower control limit (LCL) The UCL and LCL have varying degrees of importance depending on the type of chart used:

1. Accuracy Charts are generated from percent spike recovery (PSR) data and use both an upper and lower control limit. Since high accuracy is represented by 100% recovery, deviation from this value in both directions must be controlled.

2. Precision Charts are generated from the relative percent difference (RPD) between duplicate measurements and usually use only the upper control limit. Since high precision is presented by values approaching zero and differences are calculated in absolute terms, only measurements moving away from zero need to be controlled.

3. Attribute Charts are those that document the presence or absence of a certain condition. This chart is frequently used in presenting data from a series of blanks where the Y axis is the concentration of an analyte(s) to be controlled. There is no mean line calculated and the upper control limit represents the concentration of the analyte above which data would no longer be acceptable.

Out of Control: An analytical system is considered to be out-of-control if a QC measurement exceeds the control limit line on a control chart. Note that specific out-of-control definitions for each type of chart are found in the subgroup QC Protocols. The control limit is frequently predetermined by instructions in the method, and in these cases these instructions supersede the calculation of control limits by the laboratory. In setting control limits that are not predetermined, the value of 3.09 is frequently used as the constant in the formula x plus or minus ko. This represents (approximately) a 1 to 100 chance that an out-of-control point is actually part of the normal variation (a false positive). This is our default k value for all methods without predetermined control limits. In some analyses, a higher false positive rate may be accepted in order to achieve a greater degree of control. The value of 1.96 for k gives greater assurance that the system is in control, but increases the false positive rate to about 5%. Note that in all cases a normal distribution is

assumed and the minimum number of data points for establishing a working control limit is 7, but preferably 30.

Batching: Batching is used to assign samples to a specific set of QC measurements. Most methods require 5 to 10 percent of the analyses performed to be QC measurements, depending on the parameter(s) measured and the degree of control required. As a general rule, each batch of samples should have, at a minimum, an associated blank and at least one other control measurement for precision and accuracy. The size and duration of the analytical batch should be stated in the method SOP as well as the means used to document the QC measurement being part of the batch. If a specific QC measurement is determined to be out of control, all other sample measurements in the batch are considered to be out of control until corrective steps define the problem.

12.0 Laboratory Quality Assurance

Quality Assurance Procedures: Generally, two procedures are used to acquire information about how well the QA plan is operating. These are described below:

A. **Performance Evaluation Samples (PES):** These samples are defined as third party prepared check samples, whose values are known only to the third party prior to the Wastewater Management Division Laboratory submitting the results. The laboratory is aware that the samples are PES but does not have access to the true value information until after the results are submitted. In all cases, the samples are analyzed by many laboratories and the results are reported so as to reference them to overall laboratory performance. This is frequently referred to as a "Round Robin" analysis. The study is generated for compliance with all US-EPA, NELAC, NIST NVLAP, and all state technical and program requirements in effect during the study, as well as those participating in the ISO 9001 Registered Quality System. The PES, therefore, gives an independent measure of laboratory performance.

B. **Audits:** An audit is a review of all procedures used in laboratory operations to assure compliance to the written QA plan and the SOPs contained in the analytical procedures. There are two types of audits normal:

1. **Internal System Audit:** A comprehensive review of one analytical method (or a group of closely related methods) over a specific time period. This type of audit is performed by a laboratory employee who has been trained in auditing practices. The following areas may be part of a system audit.

   a. A review of the analytical results reported during a chosen time.

   b. An interview with an analyst regarding pertinent analytical SOP's.

   c. A review of analytical run logs for the chosen time period.

   d. A review of calibration data over the same time period including the source and make-up of the calibrants.

   e. A review of QC data acquired (duplicates, spikes, blanks, and spike duplicates) for the time period.

   f. A review of the QC logs to evaluate the documentation and corrective action taken for any out of control events for the method in question.

g. An assessment of how easily the above documentation is retrieved.

2. **Third Party Audits:** When necessary, the laboratory, on occasion, will call in professionals from universities or regulatory agencies to audit their control program.

Resolution of Differences:

The Wastewater Management Laboratory recognizes that even with the most technically competent programs, errors and differences will occur. When a client disagrees with the results of an analysis:

1. A check will be made for clerical errors. If none are found, go to 2. If an error is found go to 4.

2. Re-analyze samples. (If not feasible go to 5). If results reproduce, then go to 3. If an error is found, go to 4.

3. Obtain a refereed analysis at another laboratory. (If not feasible go to 5). If results reproduce then report all steps taken to indicate that the laboratory stands by the original results and that the error source is not part of the analytical system. If an error is found go to 4.

4. If an error is found in steps 1 through 3, then issue an amended report and, if the error was non-clerical, document control procedures to be taken.

5. If re-analysis or refereed analysis is not feasible, then a review of the supporting QC data is performed. If the QC data supports the original result, then this fact is reported to the client. If the QC data is weak or does not support the result, then the situation is resolved administratively.

13. <u>Laboratory Equipment and Practices:</u> This section of the QA plan addresses laboratory equipment. Method protocol and manufacturer recommendations are strictly followed to assure the equipment is functioning at optimum levels.

A. **Glassware:** All glassware used in volumetric determinations (such as pipettes and burettes) must be certified Class A for accuracy and comprised of such a material as not to interact with, or degrade with, any solution with which the glassware has contact.

B. **Balances:** The balances are the most important instruments in any laboratory because all analyses relate to weights. Gravimetric analyses are determined by two or more weights, but even the concentration-determining reagents or solutions used in volumetric analyses relate back to primary standards which are directly weighed in highly pure form and assigned a concentration based on weight. The Wastewater Management Laboratory has two Mettler AE 160 analytical balances (accurate to 0.1 mg), and one Mettler PC 4000 balance (accurate to 0.1 g.). All balances are calibrated yearly by an outside firm to certify their accuracy using Certified Class S weights. Certificates of certification are kept on file. In addition, a set of Class S

weights, in a range of 100 g. to 1 mg., is kept in the laboratory to check balances if any question arises between calibrations.

C. **Ovens:** The laboratory is equipped with two Fisher Isotemp Model 750G ovens used for drying of glassware and for solids determinations. The ovens are digitally controlled and accurate to the set point temperature plus or minus 2 degrees centigrade. Both have digital readout. In addition, the laboratory is equipped with a digitally controlled Thermolyne Type 6000 Ash Muffle used for volatile solids analysis.

D. **Biological Oxygen Demand Incubators:** The laboratory is equipped with two BOD incubators: A Precision Model 815 and a CMS Equatherm Incubator. Both are capable of maintaining temperature at 20 degrees centigrade with an accuracy of plus or minus one degree centigrade.

E. **Dissolved Oxygen Meters:** Two YSI Model 58 oxygen meters are equipped with YSI Model 5905 self-stirring probes for determining oxygen levels in BOD tests.

F. **Bacteriological Incubators:** The laboratory is equipped with two Precision coliform incubator baths and a VWR Model 1530 dry air incubator. Daily logs of temperature are kept to assure the required temperature range of plus or minus 0.2 degrees centigrade for the baths and plus or minus 0.5 degrees centigrade for the dry air incubator are observed.

G. **Autoclave:** The laboratory is equipped with a Market Forge Sterilmatic autoclave for sterilization of bacterial dilution water and other sterilizing functions.

H. **Chemical Oxygen Demand Digesters:** Two, 6-unit Glas-co heaters, designed for refluxing solutions in 300 ml., round bottom flasks are used for COD digestions.

I. **Total Kjeldahl Nitrogen Determinations:** Samples are digested using a 20-unit Fisher block digester and steam distilled using one of two distillation systems, a Kjeltec Model 1002 or Fisher Model DU 100. Acid fumes from the digestion are absorbed using a Boekel circulating aspirator bath.

J. **Spectrophotometers:** Two Milton Roy Spectronic 301 Spectrophotometers are used for colorimetric determinations.

K. **Total Organic Carbon Analyzer:** The Shimadzu TOCVcsn analyzer is equipped with an ASI Auto-sampler and a Parker BALSTON gas generator for generating "zero" air. The system is computer controlled and runs automatically, unattended.

L. **Automatic Flow Injection Analyzer:** The Lachet QC 8000 auto-analyzer is equipped with manifolds for the analysis of phosphate, nitrite plus nitrate, sulfate, chloride, and ammonia. It works in conjunction with an auto-sampler cetack ASX 500 and a RP100 series reagent pump. The system is computer controlled and runs automatically, unattended.

M. **Specific Ion Meters and pH Meters:** An Orion pH model 901 meter is used for pH analyses. Two Orion EA 940 Ion Analyzer meters are available for specific ion analyses and as backups for pH analyses.

N. **Conductance Meter:** A YSI 32 Fl conductance meter is used for de-ionized water quality control.

O. **De-ionized Water System:** The laboratory is equipped with a Barnstead Nanopure Model D4741 de-ionizer to further polish water which has already gone through a minimum of two de-ionizing tanks.

Laboratory Equipment Not Routinely Used:

A. Perkin-Elmer Model 2380 Atomic Absorption Spectrometer with Graphite Furnace.

B. Perkin-Elmer Model 500 Atomic Absorption Spectrometer with Graphite Furnace.

C. Perkin-Elmer Model 8410 Gas Chromatograph with Electron Capture Detector.

D. Perkin-Elmer Model 8500 Gas Chromatograph with Photo Ionization Detector, Hall Detector and Tekmar LSC 2000 Purge and Trap.

E. Perkin-Elmer Model 330 Scanning Spectrometer.

F. Spectronic "21" Spectrophotometer.

G. Floor Mounted Centrifuge, Model CU 500.

H. Hach Model 2100A Turbidimeter.

I. Millipore Milli-Q De-ionized water system.

J. Waters High Performance Liquid Chromatography Model 431 with conductivity, absorbance, and electrochemical detectors.

K. Dohrman Total Organic Carbon Analyzer, Model DC 80 PIR 2000 Detector.

14. Laboratory Reagents and Chemicals:

All chemicals used in the analysis of samples are ACS Reagent Grade. Any reagents used in volumetric determinations are purchased NIST certified. This includes any reagents used as spikes or quality control reagents. Laboratory reagent water is produced by passing city water through at least three cation/anion ion exchange columns with final polishing performed by a Barnstead Nanopure de-ionizer.

15. Sampling

A. Representative Sampling: A representative sample is a sample that accurately represents the concentrations of analytes, within the level of accuracy required, for each analyte of interest. Non-representative samples are of no value even if the level of analytical accuracy is beyond that required for the sample. One must define the objectives of the study and the accuracy required before a sampling design can be chosen. Sampling design is defined on basis of temporal and spatial aspects of the investigated sampling sight.

B. Spatial Aspects:

1. **Industrial Waste Sampling:** The spatial aspects of Industrial Waste Sampling are minimized by the design of the control manhole, as required by code. The design required directs all industrial effluent through a device to allow flow or time

proportioned sampling. The predetermination of a sampling sight, through which all effluent passes, minimizes the importance of spatial variation in the sampling process for industrial sampling.

2. **Environmental Sampling:** Spatial variation is generally higher in samples containing environmental contamination. Currents in flowing water and lake ecosystems must be considered if error and confidence levels are to be quantified. In lakes, stratification crucially affects the distribution of oxygen, which, in turn, affects the level of bacterial nutrients. A laboratory result which exceeds the required accuracy is of no use if the variance from spatial aspects is not known. In general, sample points with the least margin of error are those drawn in the areas of greatest turbulence and flow. Samples from stagnant pools constitute bacterial incubators which give higher bacteria counts and lower nutrient counts.

C. Temporal Aspects

1. Industrial Waste Sampling: Industrial Waste sampling is carried out to assure that relative small sub-samples of the effluent, when combined, will be representative of the waste stream as a whole. Sub-samples are taken for a 24-hour period and based either on flow (quantity) proportioned or time proportioned sub-samples. These are combined into a single analytical sample. Time proportioned samples, which exhibit a high variability, are sampled with higher numbers of sub-sampling events than those of lower variability. The magnitude of the effluent strength and the coefficient of variation between sampling events are used to determine the number of samples to be taken yearly for each company.

2. Environmental Sampling:

A. Sampling within the Storm Sewer System: This category of sampling has the express goal of the isolation and elimination of sources of contamination entering the storm sewer system. Samples are ideally taken at the center of the pipe, which represents the greatest depth and rate of flow. Care must be taken to avoid disturbance of any particulate deposits at the bottom of the pipe. Samples for bacterial analysis are taken maintaining sterile field techniques. In instances where samples cannot be accessed without confined space entry, or where flows are very low, sterile syringes are used to obtain samples. In general, any storm basin is studied from points starting upstream, and working downstream until all sources of contamination are eliminated. In instances where bacteria counts are low, but nutrient levels are high, nutrients are used as tracers to locate sources of contamination. During dry weather flow, ground water flow within the basin, at any given point, should be constant irregardless of the time of day or the day of the week. When variations in flow are observed, flow meters capable of recording flows versus time are strategically placed within the basin and used to pinpoint the location of illegal discharges. The time pattern of flow variations can constitute added evidence as to what type of entity is illegally discharging.

B. Sampling at Storm Sewer Outlets: Sampling at outlets should be carried out with the sample drawn in the upper one third of the effluent and as horizontally centered as possible. The sample should be drawn prior to any contact with areas beyond the outlet structure. If all illicit discharges in the basin have been eliminated, the outlet stream should exhibit a relative

constant analysis for all analytes of interest, over various times of the day and days of the week, during dry flow periods.

C. River Sampling: At any river sampling point, analyte concentrations vary at any given point in time. This makes any sampling point a moving target in the quest for a representative sample. In general, the most representative point to sample in stream is at the point of highest turbulence and most rapid flow. Stagnant areas act as incubators for bacteria which lower nutrient levels as the bacteria counts rise. Consequently, areas to be chosen for sampling should be as distant as possible from stagnant and slow flowing areas. Even when a proper sampling point has been chosen, a grab sample is never representative due to the analytical variance inherent with river flow. For this reason, techniques must be applied to determine levels of uncertainty and potential error inherent in a given sampling event. This is accomplished by taking a number of samples at the sampling point, equidistant apart in time, and performing a statistical workup on the analytical results for each. The following equation can be used to determine the sample's level of uncertainty or to determine the number of grab samples of equal volume to be combined into one composite sample for a given level of uncertainty for each sampling event.

$$N = 4\left(\frac{S}{\bar{x}d}\right)^2$$

S = the standard deviation of the deviations from the mean, individually calculated, for each analyte in the aliquot.

$\bar{\mathbf{X}}$ **=** the arithmetic mean of all single samples, individually calculated for each analyte in the aliquot.

N = the number of aliquots.

d = the tolerable uncertainty of the result, (e. g., 20% = 0.2).

3. Sampling Equipment:

A. ISCO GLS Samplers (7 Units): The ISCO GLS samplers are capable of being programmed with a flow meter to collect flow proportioned samples, or in a time composite mode, with or without the connected flow meter. The system uses a single 10,000 ml. bottle into which the aliquots are deposited. It lacks the ability to gather a number of individual samples.

B. ISCO 3700 Sampler (11 Units): The ISCO 3700 samplers are capable of using 24, 1000 ml. polypropylene bottles or a single 10,000 ml. container. The ISCO 3700 model can be used in conjunction with any flow meter for flow proportioned sampling, or for time based samples with or without a flow meter. Both the ISCO GLS and 3700 models can be programmed to sample a wide variety of volumes and times. The advantage of having 24 separate bottles is that multiple samples can be taken in different time intervals either based on time or flow so events such as illicit discharges, increases in flow volume, etc., can be more closely monitored and analyzed.

C. ISCO 4230 Bubbler Flow Meter (10 Units): This type of flow device is typically used with a primary measurement device such as a weir or a flume,

or another open channel flow arrangement where a known relationship exists between level and flow rate. The ISCO 4230 is capable of controlling a sampler in a flow-proportioned sampling mode. The sampler is programmed to take a sample after a specific volume of effluent has past. It is capable of printing a graph with level and flow rate, and it also indicates when a sampling event has occurred. The flow meter is also a data logger allowing the transfer of data stored in the flow meter to a personal computer.

D. ISCO 4210 Ultrasonic Flow Meter (12 Units): This type of flow meter is capable of measuring the flow rate in a large variety of open channel situations, with or without a primary device such as a flume or weir. The ISCO 4210 uses the ultrasonic method to sense level using a downward facing ultrasonic transducer. This type of meter is ideal for large sewers and can be used for applications where confined space issues arise. It is not necessary to enter manholes or vaults to install the meter because the transducer is suspended above the flow stream. Both the ISCO 4210 and 4230 models use an internal program to calculate flow rate using the depth of flow and the characteristics of the primary measuring device (weir or flume) user equation, Manning equation, etc. The ISCO 4210 has identical graphing and data logging capabilities as the 4230.

E. Sigma 950 Bubbler Flow Meter (3 Units): This type of meter, like the ISCO 4230, is designed for use with a primary measuring device (flume or weir) with a known level-to-flow relationship. The Sigma 950 series can be used with any sampler for flow proportioned sampling. It has all the capabilities of the above flow meters except the ability to graph flow data and sampling events on paper. The meter is a data logger that has an LCD display that allows the user to view data in graphic or tabular form, and it must be connected to a personal computer for data transfer and for the printing of graphs.

F. Sigma 950 Ultrasonic Flow Meter (3 Units): This type of flow meter is identical to the 950 bubbler. The only difference is the level sensing technology. It uses a downward facing ultrasonic transducer, as does its counterpart, the ISCO 4210. Like all flow meters, it may be used with any sampler.

16. <u>Safety</u>

A. Laboratory Safety: The Wastewater Management Division laboratory is committed to safe operations within the laboratory facility. As a testing laboratory, many hazardous chemicals and samples are handled daily and safety is an important aspect in the work environment. The following is a list of some essential points in the safety program.

1. **Employee Training:** All new employees, prior to beginning their work assignment, receive an introductory laboratory orientation followed by training in basis laboratory safety for each test they perform. This is carried out by an experienced, degreed chemist who is familiar with the tests involved. The training points out hazards particular to each procedure and insures that proper protective equipment is utilized. Also, this training is provided when an employee's work assignment changes or existing procedures change, which introduces a new hazard.

2. **Sample and Chemical Handling:** The Wastewater Management Laboratory makes the assumption that all samples received are hazardous, and samples are handled accordingly. It is the laboratory policy that contact with any sample or chemical used in sample analysis is to be avoided. Hoods are provided at convenient points throughout the facility for working with known or potentially hazardous materials. Any necessary personal safety equipment is provided. Any samples suspected of being particularly or unusually hazardous are placed in a hood upon login.

B. General Safety Policy: Employees of the City and County of Denver are required to abide by Executive Order Number 65 as issued by the Mayor of the City which establishes the Occupational Safety Program which states in part:

1. "As a government agency, the City does not fall under the direct authority of the Occupational Safety and Health Administration (OSHA). This Executive Order establishes a voluntary compliance program in which the City adopts OSHA standards. All departments and agencies are required to cooperate fully with the safety program. The City Attorney's Office, not OSHA, shall have the responsibility of ensuring compliance. Major portions of this order are as follows:

a. Policy

1. Provide for safe and healthful working conditions for all employees.

2. Safety is line management responsibility.

b. Safety Management

1. Compliance with the Occupational Safety and Health Act of 1970.

2. Compliance with the Uniform Building Code, the Uniform Fire Code, as well as Denver's amendments to these codes.

3. Additional policies and procedures as issued by the City Attorney's Office.

2. Department and Agency Heads shall:

a. Furnish each worker employment and a place of employment which are free from recognized hazards that may cause or are likely to cause death or serious physical harm

b. Comply with the Uniform Building Code and the Uniform Fire Code.

c. Comply with the Occupational Safety and Health Administration (OSHA), standards as listed in 29 CFR 1910 and 1926 that are applicable to the agency and with all related rules, regulations and orders.

d. Develop and implement a safety and health program in accordance with the requirements of the OSHA Act and policies and procedures proscribed by the City Attorney's Office.

e. Acquire, maintain, and require the use of approved personal protective equipment, approved safety equipment, and all other devices necessary to protect employees.

f. Ensure the submission of the budget includes appropriate resources to implement and administer effectively the agency safety and health programs.

g. Designate personnel with sufficient knowledge and training on OSHA and environmental regulations to effectively support and administrate the occupational safety and health program.

3. City Attorney's Office Shall:

a. Administer the city-wide policies and procedures on occupational safety and health and shall have the following responsibilities:

1. Develop city-wide policies and procedures on occupational safety and health and workplace environmental issues.

2. Ensure city-wide compliance with the city's Occupational Safety Program.

3. Evaluate the effectiveness of the occupational safety and health programs of departments and agencies.

b. Provide professional safety consulting services to the city's Occupational Safety Program.

c. Maintain a worker's compensation data base on employee work related injuries and disease.

4. Safety Representative Shall:

a. Integrate the safety and health program.

b. Develop necessary safety rules and regulations.

5. Supervisors Responsibilities:

a. Employees, who exercise supervisory functions shall, to the extent of their authority, furnish workers employment free from recognized hazards that may cause or could likely cause death or serious physical harm.

b. To comply with safety and health standards applicable to their agency and with rules, regulations, and orders issued by the head of the agency.

6. Employees Shall:

a. Comply with standards, rules, regulations and orders issued by the agency.

b. Use safety equipment, personal protective equipment and other devices provided or required by the agency and necessary for their protection

c. Have the right to report unsafe and unhealthful working conditions to appropriate supervisors, managers, and the city's Occupational Safety Director.

7. Failure to comply with safety rules and regulations by city employees will be cause for:

a. Administrative Action: Observance of safety rules and regulations should be reflected in the "Employee's Performance Report".

b. Progressive Discipline: Failure to observe safety regulations is cause for progressive discipline.

c. Immediate Dismissal: Failure to observe safety regulations which jeopardizes the safety of other personnel or results in major damage or destruction to property is cause for immediate dismissal.

C. Field Safety:

1. Required Equipment: In accordance with Executive Rule Number 65 and departmental safety policy, employees performing sampling duties are furnished with and expected to use the following safety equipment:

a. Required Personal Equipment

1. Steel Toed Safety Shoes

2. Coveralls

3. Hard Hats

4. Safety Vests

5. Gloves

6. Eye Protection

b. Required Vehicle Equipment

1. Emergency Flashers

2. Strobe Lights

3. Traffic Directional Indicators

4. A Minimum of 12 Traffic Cones

5. Gas Detectors

6. Blowers

7. Tripod with Wench

8. Harnesses

9. First Aid Kits

10. Fire Extinguisher

2. **Traffic Control:** Employees are trained in traffic hazard issues using the Colorado Department of Highway Flaggers Training Manual. Employees are required to protect co-workers from traffic that is passing through the sight and to protect the traveling public from dangers present by guiding traffic efficiently through the sight. The following policies and procedures have been established and implemented to decrease the dangers of traffic hazards arising during sampling from manholes in streets.

   a. Employees working in traffic are required to wear safety vests.

   b. Use of vehicle warning lights and directional signals is required.

   c. Employees are required to use traffic cones to delineate lanes and channel traffic safely around the work sight. Traffic cones are most often used to form "tapers"—sets of cones individually placed to form a line which is used to channel traffic into unimpeded lanes. Traffic cones are placed using the "minimum desirable taper length formula" for transitions:

      1. For speeds of 45 mph or greater, $L = (S)(W)$, where L = the minimum desirable length of the taper, S = the value of the speed limit or 85% of the speed, and W = the width of the offset.

      2. For speeds of 40 mph or less, $L = (W)(S^2)/(60)$.

3. **Confined Space Entry:** The atmosphere in a confined space may be extremely dangerous due to the lack of air movement. This procedure has been developed to ensure employees recognize confined space and take the necessary precautions before entering a confined space. The hazards which might be encountered are 1) oxygen-deficient environment, 2) flammable atmospheres, 3) toxic atmospheres and 4) physical hazards such as electric lines or standing water. Before confined spaces are entered, the air must be tested to determine whether or not a hazardous atmosphere is present. In accordance with this procedure, a Confined Space Permit must be completed before a confined space entry is made.

   a. **Definitions:**

1. **Atmospheric Testing—**The use of a monitoring device to test the air in a confined space to ensure that the oxygen concentration is between 19.5 – 23.5%, combustible gases are below 10% LEL, and toxic gases are below 50% TLV.

2. **Attendant—**An individual stationed outside a confined space who monitors the entrant's safety

3. **Confined Space—**Any space that is large enough and so configured that an employee can bodily enter and perform assigned work, has limited openings for entry and exit, has a lack of ventilation, contains known or potential hazards, and is not intended for continuous human occupancy. Examples of confined space are manholes, vaults, pits, tanks, storage bins, etc.

4. **Confined Space Entry Permit—**A pre-formatted and written document that must be completely filled out before entering a confined space. The permit requires information on atmospheric testing, names of entrants, location of confined space, and emergency response.

5. **Lower Explosive Limit (LEL)—**The lower limit of flammability of a gas or vapor at ordinary ambient temperatures expressed in percent of the gas or vapor in the air by volume.

6. **Oxygen Deficient Atmosphere—**An atmosphere containing less than 19.5% oxygen by volume.

7. **Retrieval System—**The equipment (including a retrieval line, full body harness, and a lifting device) used for non-entry rescue of persons from a confined space.

8. **Threshold Limit Value (TLV)—**A term used to express the airborne concentration of any material to which nearly all persons can be exposed day after day, without adverse effects.

b. **Regulatory Compliance—**Before entering a confined space, a blank Confined Space Entry Permit must be obtained from the unit supervisor, safety coordinator, or from the City Attorney's Office. A blank permit is also attached at the end of this procedure that can be photocopied. The permit should be filled out as the following steps are completed.

1. Any conditions making it unsafe to remove an entrance cover shall be eliminated before the cover is removed.

2. When the entrance cover is removed, but before an employee enters the space, the internal atmosphere shall be tested, with a calibrated direct-reading instrument, for the following conditions in the order given:

    a. Oxygen content

    b. Flammable gases and vapors

c. Potential toxic air contaminants

3. Employees may not enter the space if the atmosphere is hazardous until continuous forced air ventilation is used to eliminate any hazardous atmosphere.

a. Forced air shall be so directed as to ventilate the immediate areas here an employee is or will be present within the space and shall continue until all employees have left the space.

b. The air supply from the forced air ventilation shall be from a clean source and may not increase the hazards in the space.

c. The atmosphere within the space shall be continuously tested as necessary to ensure that continuous forced air ventilation is preventing the accumulation of a hazardous atmosphere.

d. If a hazardous atmosphere is detected during or after entry:

1. Each employee shall leave the space immediately.
2. The space shall be evaluated to determine how the hazardous atmosphere developed.
3. Measures shall be implemented to protect employees from the hazardous atmosphere before any subsequent re-entry takes place.

e. A communication device such as a telephone (cellular or hardwired) or a two-way radio must be available for use in the event of an emergency.

f. To expedite rescues, in the event of an emergency, all entrants must wear a full body harness at all times while in a confined space.

b. Duties and Responsibilities:

1. **Department Heads, Managers, and Supervisors** shall ensure that all employees are properly trained and that the necessary safety equipment is available to workers whose work assignments include entry into confined space. Workers shall not be assigned or allowed to enter a confined space without the following equipment:

a. An atmospheric monitor to measure oxygen concentration, any presence of combustible gases, and any presence of toxic gas

b. A mechanical ventilation device.

c. Emergency communication equipment.

d. Full body harness for all entrants.

2. **The Entrant** shall ensure that all necessary preliminary steps are taken including the completion of a Confined Space Entry Permit before making entry. Entrants shall not enter confined spaces if they are not properly trained or if the space is unsafe. Entrants have the following responsibilities:

   a. Know the hazards that may be faced during entry.

   b. Properly use the safety equipment.

   c. Communicate with the attendant as necessary to enable the attendant to monitor the entrant's status and to enable the attendant to alert entrants of the need to evacuate the space if the atmosphere becomes hazardous.

   d. Alert the attendant whenever the entrant recognizes any symptoms of exposure to a dangerous situation.

   e. Exit the space as quickly as possible whenever ordered to by the attendant, if a dangerous situation is identified, or if an evacuation alarm is activated.

3. **Attendants** shall be assigned to remain outside of the confined space and to be in constant contact (visual or speech) with the worker(s) inside. The attendant shall not have any other duties which could distract him/her from monitoring the workers in the space and shall know who to contact in the event of an emergency. Attendants shall have the following responsibilities:

   a. Know the hazards that may be faced during entry.

   b. Be aware of possible behavior effects of hazardous exposure to entrants.

   c. Maintain an accurate count of the number of entrants in the space at all times.

   d. Remain outside the permit space at all times until relieved by another attendant.

   e. Communicate with entrants as necessary to monitor entrants' status and to alert them of the need to evacuate if conditions become hazardous.

   f. Monitor the activities inside and outside the space to determine if it is safe for the entrants to remain in the space and order an immediate evacuation if dangerous conditions develop.

g. Summon rescue and other emergency services as soon as the attendant determines that the entrants may need assistance to escape from the space.

h. Ensure that unauthorized persons do not enter the space.

i. Perform no duties which might interfere with the attendant's primary duty to monitor and protect the entrants.

4. Emergency and Rescue Procedures: Rescues in confined space will be performed by the Denver Fire Department. To ensure timely rescue, the following requirements have been established:

a. The Denver Fire Department shall maintain the required equipment to perform confined space rescues and ensure that fire department personnel are properly trained on the hazards of confined spaces and rescue techniques.

b. City work crews shall have a means of communication readily available prior to entering a confined space. A two-way radio or telephone must be immediately accessible to the attendant so that there will be no delay in reporting an emergency situation.

c. Confined space entrants shall wear a full body harness at all times when in a confined space. The harness shall be equipped with a connecting ring on the back, between the shoulders, so that a rescue line can be quickly attached in the event of an emergency.