



Rifle Creek Watershed Assessment - Sampling and Analysis Project Plan

Middle Colorado Watershed Council
-Contracting Entity

December 12, 2016

Nonpoint Source Project Manager

Date

Nonpoint Source Project Quality Assurance Officer

Date

CDPHE NPS Program Coordinator

Date

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A - Project Management

A-3 – Distribution List

Name	Project Title / Responsibility
Middle Colorado Watershed Council Board of Directors - Donna Gray (Board President)	Stakeholders Group – Middle Colorado Watershed Council (MCWC)
Laurie Rink (MCWC Director)	Project Manager
Nate Higginson (MCWC Watershed Specialist)	Project QA Officer / Sampling Leader / Laboratory Manager

A-4 – Problem Background – Sampling Needs

The Rifle Creek Watershed is approximately 200 square miles in size and contains 61 linear miles of stream. The major named drainages include the mainstem of Rifle Creek, the Middle, East and West forks of Rifle Creek, and Government Creek. Rifle Gap Reservoir is located near the confluence of the Middle, East and West forks of Rifle Creek. The headwaters originate in the White River National Forest at an elevation of approximately 9,200 feet and flow south to the confluence of Rifle Creek with the Colorado River at the City of Rifle at about 5,300 feet (See Figure 1 in Appendix 1). Much of the private land is used for agricultural purposes.

Table 2-1 Land Areas in the Rifle Creek Watershed

Watershed	Land Area (mi ²)	Land Area (% of Total)
Mainstem Rifle Creek	21.0	10.5%
East Rifle Creek	57.8	28.8%
Middle Rifle Creek	43.2	21.6%
West Rifle Creek	33.5	16.7%
Government Creek	44.9	22.4%
Total Rifle Creek Watershed	200.4	100.0%

Table 2-2 Land Ownership in the Rifle Creek Watershed

Jurisdiction	Land Area (mi ²)	Land Area (% of Total)
Bureau of Land Management	94.8	47.3%
Bureau of Reclamation	2.1	1.0%
Department of Defense	0.3	0.1%
Local Governments	2.5	1.2%
Private	56.6	28.2%
United States Forest Service	44.1	22.0%
Total Rifle Creek Watershed	200.4	100.0%

In 2012 West Rifle Creek, East Rifle Creek and the mainstem of Rifle Creek below Rifle Gap Reservoir were listed on the 303(d) List of Impaired Waters published by the Colorado Department of Public Health and Environment (CDPHE) for selenium. During sampling conducted from August 2006 to June 2007, in Rifle Creek about a mile upstream of its confluence with the Colorado River, one sample exceeded the chronic standard for selenium, five did not exceed that standard. West Rifle Creek was also listed in 2012 for total recoverable iron on the Monitoring and Evaluation List. It became apparent that data needed to be collected in Rifle Creek and its tributaries in order to further assess this watershed and the sources of pollution.

The Middle Colorado Watershed Council (MCWC) began sampling in 2015 in order to assess the extent and severity of selenium and other pollutants. 13 sites were sampled in 2015 and 2016. While these data were being collected, an updated 303(d) list was being developed. As of 2016, this watershed is no longer listed for selenium. All of the Rifle Creek watershed is now listed for arsenic and for E. coli on the Monitoring and Evaluating (M&E) list. West Rifle Creek is on the M&E list for total iron, dissolved iron, and sulfate.

The parameters of specific interest may have changed for this project but the goal remains the same. The goal is to collect water quality data in the basin where the streams support irrigation, recreation and aquatic life. This goal aligns with the mission of the Middle Colorado Watershed Council (MCWC) which is to protect and enhance watershed health. The MCWC will be administering this project and analyzing the resulting data. It is hoped that data will reveal whether detected pollutants arise from natural processes, are due to specific land uses, or some combination.

Besides the MCWC, these data will be used to inform stakeholders including: federal land managers (BLM and US Forest Service), Colorado Parks and Wildlife, private landowners, and county / municipal governments. With the help of this information Best Management Practices (BMPs) will be selected and implemented.

Problem Statement:

The Rifle Creek Watershed is an area of concern for local residents and stakeholders. The 303(d) listing of this stream makes further investigation of water quality a high priority.

Intended Use of Data:

To better describe surface water quality and potential sources of nonpoint source (NPS) pollution. Accordingly, the results of the data analysis will help characterize suspected nonpoint sources of pollution both spatially and seasonally to best inform the use of Best Management Practices (BMPs) by land managers. Selenium, arsenic, total recoverable iron, and nitrate are the parameters of particular concern for this project based on current and past state 303(d) evaluations.

A-5 -- Task Description

a. -- General Overview of Project

Stream surface water will be sampled and analyzed for various parameters. Parameters on the 303(d) and the Monitoring and Evaluating list will be given high priority. Certain measurements will be taken in the field and at the same time and location as collected laboratory samples. These samples and measurements will take place at various representative locations throughout the Rifle Creek Watershed (see A-6b, Sampling Project Locations).

The following parameters will be measured at each sampling location:

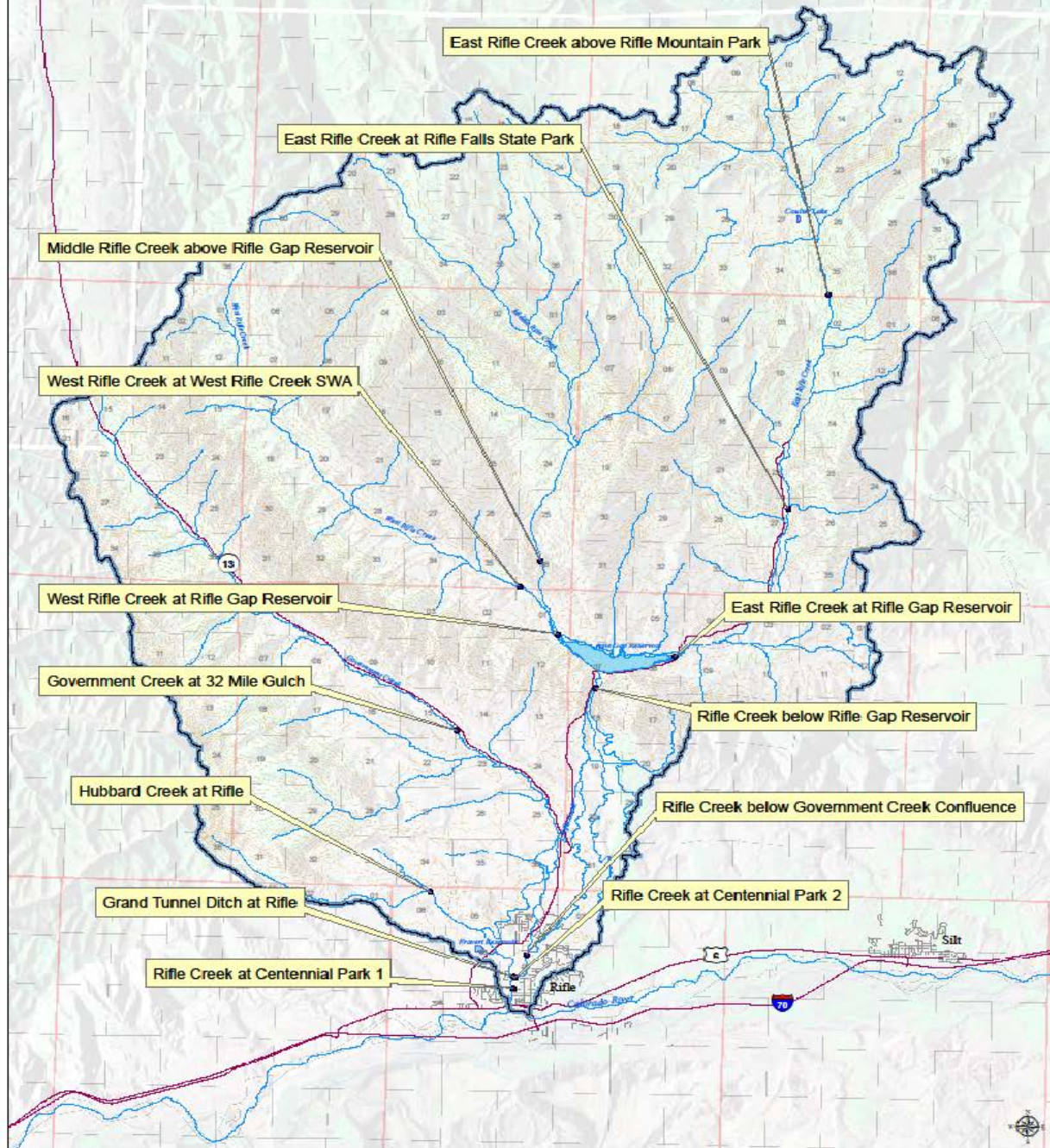
1. Temperature (water and air)
2. Dissolved Oxygen
3. pH
4. Alkalinity
5. Hardness
6. Metal Concentrations
 - a) Aluminum (Al)
 - b) Arsenic (As)
 - c) Cadmium (Cd)
 - d) Calcium (Ca)
 - e) Copper (Cu)
 - f) Iron (Fe)
 - g) Lead (Pb)
 - h) Magnesium (Mg)
 - i) Manganese (Mn)
 - j) Potassium (K)
 - k) Selenium (Se)
 - l) Sodium (Na)
 - m) Zinc (Zn)
7. Ammonia (NH₃)
8. Nitrite (NO₂) and Nitrate (NO₃)

Of these measurements and parameters selenium, arsenic, iron, and sulphate are of greatest concern due their presence on the 303(d) list. These four parameters will be compared to CDPHE Standards for the Rifle Creek Watershed. 303(d) standards are to be obtained from CDPHE Regulation 93 for Rifle Creek (Upper Colorado Segment 10). The other parameters will be examined will be considered secondary, but will still be evaluated.

b. -- Sampling Project Locations

See map below:

**Rifle Creek Watershed Assessment
Sampling Locations**



0 0.5 1 2 3 4 5 6 Miles 1:110,000 1 inch on the map represents 2 miles on the ground 0 0.5 1 2 3 4 5 6 7 8 9 10 Kilometers

- Legend**
- Streams
 - Roads
 - Watershed Boundary



Source: CDOT, USGS, Colorado Riverwatch

Site ID	Description	Waterbody Name	Notes	Latitude	Longitude
1	Rifle Creek at Centennial Park 1	Rifle Creek	Rifle Creek in Centennial Park below the confluence with Grand Tunnel Ditch	39.5345	-107.79
2	Grand Tunnel Ditch at Rifle	Grand Tunnel Ditch	Grand Tunnel Ditch in Centennial Park	39.5380	-107.7852
3	Rifle Creek at Centennial Park 2	Rifle Creek	Rifle Creek in Centennial Park above the confluence with Grand Tunnel Ditch	39.5378	-107.7849
4	Hubbard Creek at Rifle	Hubbard Creek	On BLM land upstream of USFS Ranger Station	39.5622	-107.8143
5	Rifle Creek below Government Creek	Rifle Creek	At Rifle Skate Park	39.5447	-107.78
6	Government Creek at 32 Mile Gulch	Government Creek	Off BLM Road 8051, on south side of Hwy 13 SE of Rifle Arch Trailhead	39.6096	-107.8075
7	Rifle Creek below Rifle Gap Reservoir	Rifle Creek	On Rifle Creek on State Park land at the Christo Day Use Area	39.6229	-107.7613
8	West Rifle Creek at Rifle Gap Reservoir	West Rifle Creek	Park at the swim beach and walk along service road west approximately 1/2 mile to reach West Rifle Creek	39.6386	-107.7741
9	Middle Rifle Creek	Middle Rifle Creek	On BLM land 1 mile north of Rifle Correctional Facility	39.6597	-107.7813
10	West Rifle Creek at West Rifle Creek SWA	West Rifle Creek	Spur road on south side of Hwy 252 approximately 1/2 mile west from the intersection with Hwy 219, access gate to the SWA	39.6517	-107.7882
11	East Rifle Creek at Rifle Gap State Park	East Rifle Creek	At the pedestrian bridge in Rifle Gap State Park	39.6326	-107.7353
12	East Rifle Creek at Rifle Falls State Park	East Rifle Creek	In channel directly downstream of Rifle Falls before diversion	39.6767	-107.6983
13	East Rifle Creek above Rifle Mountain Park	East Rifle Creek	Access from USFS Kiosk north of Rifle Mountain Park	39.7396	-107.6879

III – Sampling Project Timetable

Sampling Timeline Overview & Responsibilities						
Activity	Method	Locations	Sampled-to-Date	Future Sampling	Anticipated Date of Completion	Responsible Party(s)
Water chemistry sampling (all parameters)	River Watch	All (see map)	Aug, Oct 2015; May, Oct 2016	May, Aug, Oct 2017	October 2017	N. Higginson - with assistance

A-6 - Data Quality Objectives for Measurement Data

The data quality objectives for this project are the same as the standards used by River Watch, which are the same standards presented in the Water Quality Control Division’s Quality Assurance Project Plan (see Appendix 1 for reference).

a. Data Precision, Accuracy and Measurement Range:

Data precision, accuracy, and measurement range are all tied directly to River Watch, which dictates all of the methods and corresponding data Quality Assurance Project Plan (QAPP). River Watch is currently using the Water Quality Control Division’s (WQCD) QAPP, therefore, all quantitative standards match WQCD standards for all of the parameters listed in section A-6.

It was determined that private laboratories are need for an increased level of detection as well as accuracy and precision. Method detection limits (MDL) is the lowest non-zero concentration that can be measured with a high degree of confidence, but the exact concentration cannot be determined reliably. Parameters which are of greatest importance and thus require special scrutiny include: selenium, arsenic, iron, and sulfate. Precision and accuracy of this data will be obtained from private laboratories utilized.

b. Data Representativeness:

Stream samples will be collected as composite samples to ensure they are representative. Composite sample will consist of 1/3 taken from the left bank, 1/3 taken from the thalweg (the line of fastest flow in the stream channel and often the deepest), and 1/3 taken from the right bank. If stream conditions are unsafe for the sampler to wade into the thalweg, the sample may be made from the stream bank where active flow occurs (called a grab sample), or a composite sample can be taken from a bridge using a rinsed bucket.

Timing

Spring, late summer, and fall sampling were chosen in order to be assess different flow regimes and to capture potential effects of differing land management. Spring sampling aims to catch spring runoff. Summer sampling is conducted to catch surface water return irrigation flows and any contaminants that may come with it. Fall data collection is to capture low flow conditions and possible effects of groundwater irrigation return flows.

Site Selection

Sample sites were selected to characterize the watershed from top to bottom, including its various tributary. Sites were selected based on their relation to potential disturbances as well as based on accessibility. For example, a site was placed on the mainstem of Rifle Creek below Rifle Gap Reservoir and multiple sites were selected in the town of Rifle.

c. Data Comparability:

Field staff have been trained in data collection techniques through River Watch of Colorado. The program provides high-quality training to certify individuals as qualified data collectors. River Watch uses standard units to ensure comparability and establishes appropriate accuracy and precision for sample analysis. The program is widespread – ensuring comparability of this data with similar studies of streams throughout the state of Colorado.

d. Data Completeness:

According to the WQCD QAPP:

Completeness is the percentage of all data collected which are acceptable. For example, data may become unusable due to laboratory error, holding time violations, or errors in field collection procedures. A target of 90% completeness will be considered acceptable. To be considered complete, the data set must contain all QC check analyses verifying precision and accuracy for the analytical protocol. Completeness is then determined by the following:

$$\% \text{ Completeness} = (\text{Number of Valid Measurements} / \text{Total Number of Measurements Planned}) \times 100$$

A-7 -- Training Requirements and Certification

All field staff have completed the River Watch of Colorado training and received their certification. At least one person who received this training and certification will be present at sampling events. This person will lead training of assisting personnel present at the time of sampling, as necessary.

River Watch is a program sponsored by Colorado Parks and Wildlife and the Colorado Watershed Assembly (CWA). Its mission is largely educational, but this program focuses on collecting high-quality data that can inform citizens as well as decision makers.

A-8 -- Documentation and Records

Field Data Collection

All field staff will document water quality monitoring activities using a field log notebook on Rite-in-the-Rain™ waterproof paper when available. All field notes will be transferred to pre-printed field data sheets (Appendix 2). Each sampling event will have its own data sheet that will include all pertinent data as requested on the form. Each entry will include at least the following: sample date and time, site number and description, sample collector's name(s), site latitude and longitude and associated GPS documenting data, how and where the sample was collected (e.g. directly out of the stream, out of a bucket), weather conditions, sample filtering information, observations and comments and summary of quality assurance and quality control (QA/QC) activity, if any.

Field entries will be dated, legible, preferably made in black indelible ink, and contain accurate documentation. Corrections to erroneous data will be made by crossing through the entry and entering the correct information. The person making the correction will initial and date where the error occurred.

Sample Labeling

Every sampling event will have a unique identification number (UIN). Individual sample bottles will have a self-adhesive label affixed to the exterior of each bottle set prior to a given sample trip. The UIN consists of a combination of station number, sample date and sample time in 24-hour format. The first three numbers refer to the station number. The next eight numbers refer to the date (xx/xx/xxxx will equate to xxxxxxxx). The final four digits refer to the time. Each sampler will be responsible for making sure that each number used in their block is unique. The sampling leader will double check this labeling.

Data Sheets

All data collected during sampling events will be entered onto River Watch of Colorado data sheets (Appendix 2). All data sheets will be scanned and stored on the Project Drive at Middle Colorado Watershed Council/CurrentProjects. Geospatial data will be projected into the coordinate system UTM Zone 13N based on the NAD 1983 datum. All data sheets will be sent with metals and nutrients samples to River Watch with a chain-of-custody form.

B - Measurement / Data Generation and Acquisition

B-1 - Sampling Process Design

Timing

Spring, late summer, and fall sampling were chosen in order to assess different flow regimes and to capture potential effects of differing land management. Spring sampling aims to catch spring runoff. Summer sampling is conducted to catch surface water return irrigation flows and any contaminants that may come with it. Fall data collection is to capture low flow conditions and possible effects of groundwater irrigation return flows.

Site Selection

Sample sites were selected to characterize the watershed from top to bottom, including its various tributary. Sites were selected based on their relation to potential disturbances as well as based on accessibility. For example, a site was placed on the mainstem of Rifle Creek below Rifle Gap Reservoir and multiple sites were selected in the town of Rifle. Many of these sites were selected because they had been sampled previously.

In the case of unsafe sampling conditions sampling will be delayed or methods detailed in section A-9b will be employed (grab sample).

B-2 -- Sampling Methods

The following parameters will be measured at each sampling location:

1. Temperature (water and air)
2. Dissolved Oxygen
3. pH
4. Alkalinity
5. Hardness
6. Metal Concentrations
 - a) Aluminum (Al)
 - b) Arsenic (As)
 - c) Cadmium (Cd)
 - g) Calcium (Ca)
 - h) Copper (Cu)
 - i) Iron (Fe)
 - d) Lead (Pb)
 - e) Magnesium (Mg)
 - f) Manganese (Mn)
 - j) Potassium (K)
 - k) Selenium (Se)
 - l) Sodium (Na)
 - m) Zinc (Zn)
9. Ammonia (NH₃)
10. Nitrite (NO₂) and Nitrate (NO₃)

Sample Preparation

Sample bottles will be prepared and labeled prior to any sampling event. Before all sample collections, the following steps will be taken:

1. A specific sampling plan will be developed, determining which stations will be sampled during the day.
2. In the lab, soak the pH probe in KCL solution. (if not using electronic meter)
3. If metals are to be collected, prepare all sample bottles as follows:
 - a) Pre-fix all metals samples with 12 drops HNO₃.
 - b) Every 5th sample collected will have a blank and duplicate sample associated.
 - c) Blank samples are to be filled with DI water.
 - d) Label bottles as appropriate.
4. If nutrients are to be collected, prepare all samples as follows:
 - a) Bring materials for a nutrients duplicate if appropriate to do so (instructions for nutrients duplicates will be provided by River Watch).
 - b) Label bottles as appropriate.

Measurements Made in the Field

Field measurements for temperature, conductivity, specific conductance, salinity and dissolved oxygen (DO) will be made when water chemistry samples are collected. These parameters will be measured using YSI Model 85 and YSI Model 63 handheld meters. The YSI Model 85 will be used for DO only. The YSI Model 63 will be used to measure temperature, conductivity, specific conductance, and salinity.

In the case where the YSI meters are unavailable, samples will be collected and analyzed for in the lab for pH and DO. Temperature will be taken using a generic thermometer.

A 16 oz. bottled sample will be taken from each station for laboratory analysis of alkalinity and hardness. All stream samples will be collected as composite samples (excluding DO if taken this way) to ensure they are representative. Composite samples will consist of 1/3 taken from the left bank, 1/3 taken from the thalweg (the line of fastest flow in the stream channel and often the deepest), and 1/3 taken from the right bank. If stream conditions are unsafe for the sampler to wade into the thalweg, the sample may be made from the stream bank where active flow occurs (called a grab sample), or a composite sample can be taken from a bridge using a rinsed bucket.

A Marsh-McBirney flow meter will be used to estimate flow using three measurements. These measurements are taken at 1/4, 1/2, and 3/4 across the stream width. Once taken, these measurements will be averaged to obtain “v” in the equation shown above. Depth will be taken at the same intervals and averaged as well.

In the instance where a flow meter is unavailable, velocity will be calculated by floating an object over a measured distance and recording time. Travel distance will be divided by travel time. There may be instances where a calculation of stream discharge will not be possible with a flow meter or a floating object due to low volumes. In these instances, a portable weir plate will be used.

Stream discharge, measured in cubic feet per second (CFS), will be calculated using the following equation (see Appendix 2 for data sheet):

$$\text{Discharge (Q)} = v * w * d * a$$

Where:

v = velocity of the stream measured with a Marsh McBirney Flow Meter, in feet per second

w = average width of the channel section in feet

d = average depth in feet

a= A coefficient to account for friction along the stream bottom (0.8 for rocky-bottom streams and 0.9 muddy-bottom streams)

Measurements Made in the Lab

Once in the lab, all metals and nutrients bottles will be immediately refrigerated. With collected sample bottles, measurements will be made for alkalinity, hardness, pH and dissolved oxygen (if meter is unavailable). Alkalinity, hardness and DO will be hand titrated according to the procedures outlined in the *River Watch of Colorado Water Quality Sampling Manual*. Sample holding time for DO is 8 hours, and alkalinity/hardness is 24 hours. All data

will be recorded on appropriate data sheets and submitted with metals and nutrients samples to River Watch of Colorado.

Certain parameters are to be measured by private laboratories as well as River Watch. These included: selenium, arsenic, iron, and sulphate. These parameters were those included in 303(d) and Monitoring and Evaluation lists in this area and were therefore of special importance. Private laboratories are to be employed due to providing results faster and being better able to detect lower concentrations.

a. Sampling Needs

Containers, Preservation Techniques, and Holding Times of Various Parameters

Parameter	Matrix	Sampling Procedures (a)	Sample Container	Sample Preservation	Holding Times
Temperature	Water	Composite	N/A	N/A	N/A
Dissolved Oxygen	Water	Composite	N/A	N/A	8 hours
pH	Water	Composite	N/A	N/A	24 hours
Alkalinity	Water	Composite	16oz Sample Bottle	N/A	24 hours
Hardness	Water	Composite	16oz Sample Bottle	N/A	24 hours
Metals	Water	Composite	Sample Bottle	Nitric Acid / Refrigerate	6 months
Nutrients	Water	Composite	Sample Bottle	Sulfuric Acid	48 hours
Total Suspended Solids	Water	Composite	Sample Bottle	N/A	48 hours

b. Equipment Needs

Each sampling location will have its own set of sampling bottles. This will eliminate cross-contamination between sites. At the site, all sampling containers will be rinsed with deionized water once and sample water twice. The exceptions to this being metals bottles and nutrient bottles, which contain preservatives. All equipment used at multiple sites will be rinsed / cleaned thoroughly. Laboratory equipment is cleaned with deionized water, then sample water before being used to conduct the test. Following the execution of the test (i.e. alkalinity), the equipment is then cleaned once with acid to remove films, followed by a deionized water rinse.

The YSI Model 85 Handheld Meter is calibrated at the beginning of every sampling event. This ensures accurate readings. Calibration is to be documented on a sheet for each instrument. Readings are taken when they have settled on a value for an acceptable amount of time, therefore eliminating the possibility of the previous site sample influencing the reading.

B-3 -- Sample Handling and Custody

Sample Labeling

Every sampling event will have a unique identification number (UIN). Individual sample bottles will have a self-adhesive labels affixed to the exterior of each bottle set prior to a given sample trip. The UIN consists of a combination of station number, sample date and sample time in 24-hour format. The first three numbers refer to the station number. The next eight numbers refer to the date (xx/xx/xxxx will equate to xxxxxxxx). The final four digits refer to the time. Each sampler shall be responsible for making sure that each number used in their block is unique.

Samples will be handed over to the sampling leader after the sites sampling event is complete. It is then up to the sampling leader to double-check labeling before sending off samples for metals and nutrients to the proper location. All nutrient samples are required to be refrigerated. Holding times must be adhered to as well (See section B-2a). Secure packaging, adequate dry ice for nutrient samples, and samples that are not overly full (to allow for expansion) will ensure that samples reach their destination at the lab in good condition. Data sheets and a chain-of-custody form (See Appendix 2) are required to accompany all samples sent to River Watch's lab as well as any private laboratory used.

All field data will be recorded initially via Microsoft Excel. This will be done by the sampling leader, who will check data for feasibility as entered. Additionally, all field collected data will be entered online into River Watch's and to the Colorado Data Sharing Network (CDSN) via the Aquatic Water Quality Monitoring System (AWQMS) database.

B-4 -- Analytical Methods Requirements

River Watch Reporting Limits and Methods by Parameter:

Metals

Parameter	Reporting Limit	Method
Aluminum	15 ug/l	EPA 200.7 (ICP)
Arsenic	15 ug/l	EPA 200.7 (ICP)
Calcium	100 ug/l	EPA 200.7 (ICP)
Cadmium	0.15 ug/l	EPA 200.7 (ICP)
Copper	1 ug/l	EPA 200.7 (ICP)
Iron	10 ug/l	EPA 200.7 (ICP)
Magnesium	100 ug/l	EPA 200.7 (ICP)
Manganese	5 ug/l	EPA 200.7 (ICP)
Lead	3 ug/l	EPA 200.7 (ICP)
Selenium	5 ug/l	EPA 200.7 (ICP)
Zinc	3 ug/l	EPA 200.7 (ICP)
Potassium	100 ug/l	EPA 200.7 (ICP)
Sodium	200 ug/l	EPA 200.7 (ICP)

Nutrients

Parameter	Reporting Limit	Method
Sulfate	0.5 mg/l	EPA 375.4
Chloride	1 mg/l	EPA 325.1
Total Suspended Solids	4 mg/l	NA
Ammonia	0.01 mg/l	EPA 350.1
Nitrate + Nitrite	0.02 mg/l	EPA 353.2
Total Phosphorus	0.005 mg/l	EPA 365.1 & 365.3

Field Parameters

Parameter	Reporting Limit	Method
pH	0.01 S.U.	NA
Dissolved Oxygen	0.5 mg/l	SM 421 B
Alkalinity	2 mg/l	EPA 310.1
Hardness	2 mg/l	SM 314.B

B-5 - Quality Control Requirements

a. Field QC Checks:

Duplicate and blank samples for metals will be taken every fifth sampling event. These are samples that are taken with the same equipment at the same time. One syringe will be used to fill two metals bottles half way, alternating 10ml at a time. The same procedure will fill the sample bottles the rest of the way. Ten percent of nutrient samples are duplicated in a similar manner, although they are taken without a syringe.

Site visits are to be conducted once per year by River Watch to test equipment chemicals, and training of the MCWC personnel sampling. During a visit River Watch employees provide a sample of known field-tested parameters (alkalinity, hardness, and pH) and have the MCWC representative test the known sample for these parameters. Dissolved oxygen (DO) measurement is tested by being able to produce similar results from two tests of the same water. Additionally, River Watch employees test the equipment by evaluating alkalinity, hardness, pH, and DO of a sample using MCWC equipment checked against a second set of equipment.

b. Laboratory QC Checks:

Of primary focus for this project are concentrations of selenium, arsenic, total iron, and sulfate. For this reason, duplicate samples will be sent to a private lab (ACZ Laboratories and/or Grand Junction Laboratories) to test for these parameters with greater accuracy. A

request will be made for the laboratory to check its results and provide precision and accuracy ranges.

With the exception of the parameters noted above, quality control will be completed by River Watch of Colorado utilizing the Colorado Water Quality Control Division's (WQCD) Quality Assurance Project Plan (QAPP) (See Appendix 1 for reference).

c. Data Analysis QC Checks:

Any data not meeting the standards put forth in the WQCD QAPP will be qualified and flagged or thrown out as deemed necessary. Any data not properly checked for quality assurance by the laboratory will also be qualified in the project's results.

B-6 - Equipment Testing, Calibration, Inspection and Maintenance

Duplicate samples will be used to test the equipment. Site visits, which are conducted once a year, also test the equipment. See section B-5a for descriptions. If duplicate samples and site visits reveal equipment is causing data to fail to meet quality objectives, the faulty equipment will be replaced.

All gear is cleaned before sampling as well as after sampling. This redundancy reduces the chances of contamination. Cleaning before sampling is done with deionized water twice and sample water twice. After the sample is collected, any equipment that will be used at another site will be cleaned with diluted nitric acid to eliminate any metals or nutrients that may have stuck to the inside of the container (mainly syringe). After this acid rinse a regular deionized water rinse will follow. Site visits by River Watch serve to double check sampling personnel's methods and calibrate their techniques as well. They will quiz the sampling leader on his/her sampling knowledge. This ensures constant retraining of personnel so that data quality remains high.

All electronic equipment will be calibrated before each sampling event. This includes the YSI Model 85 and YSI Model 63 meters. pH equipment is calibrated using pH standards of 7 and 10, which bracket the expected pH range. Likewise, solutions are used for calibration of conductivity and salinity. This calibration will be recorded by the sampling leader and kept in the case along with the electronic meters.

B-7 -- Inspection / Acceptance Requirements for Supplies

During the River Watch training, MCWC staff were provided with lists of required supplies and MCWC's stock of these supplies was inventoried and refilled as necessary. Additional supplies needed for shipping and to send duplicate samples to a laboratory will be double-checked prior to each sampling event.

B-8 - Data Acquisition Requirements

Discharge estimates are obtained for this study at each sampling location. When available, additional discharge data may be obtained and used for Total Daily Maximum Load (TDML) calculations. These data will be accessed via Colorado's Division of Water Resources (DWR) website: <http://www.dwr.state.co.us/SurfaceWater/data/division.aspx?div=5>. Any provisional data will be noted as such if used in reports.

Historical data from past sampling will be accessed via River Watch and CDSN databases for comparison to recent findings. This data will be properly labeled as different from the new data collected in 2017.

B-9 - Data Management

All field staff will document water quality monitoring activities using a field log notebook on Rite-in-the-Rain™ waterproof paper when available. All field notes will be transferred to pre-printed field data sheets. Each sampling event will have its own data sheet and include all pertinent data requested on the form. Each entry will include at least the following; sample date and time, site number and description, sample collector's name(s), site latitude and longitude and associated GPS documenting data, how and where the sample was collected (e.g. directly out of the stream, out of a bucket), weather conditions, sample filtering information, observations and comments and summary of quality assurance and quality control (QA/QC) activity, if any. Before leaving a site, the field data sheet will be checked to make sure all fields are filled in and proper labels are affixed to each sample bottle.

Once sampling personnel are back from the day of sampling, tests for alkalinity and hardness will be completed. These will have their own data sheets which are subsequently checked for completion after the tests are completed. Any suspect tests are redone with remaining sample water.

Data is then ready for electronic entry into a Microsoft Excel spreadsheet. This will allow another opportunity to double-check numbers. All calculations will be also be cross checked at this time.

Metals and nutrients are sent to River Watch as well as a private laboratory (for certain parameters) for analysis before the holding times expire. If holding times are surpassed, samples will be discarded or data will be qualified. Before shipping, all labels are double-checked for completeness and accuracy. Nutrient samples will be shipped in coolers with appropriate amount of dry ice.

Data will be uploaded to CDSN and EPA via the Water Quality Data Exchange (WQX, also known as STORET). Submission to the EPA will be done via the Ambient Water Quality Monitoring System (AWQMS) at: <https://awqms.goldsystems.com/Login.aspx>.

This data upload will involve:

- Preparing the Data File for Import
- Creating an Import Configuration

- Import the Data
- Resolve Validation Errors
- Migrate the Dataset into the AWQMS database
- Export / Submit the Dataset to WQX

Detailed instruction on this process can be viewed at:

<https://awqms.goldsystems.com/download/AWQMS%20User%20Guide.pdf>.

The status of the submission to the EPA will be double checked by viewing the “Complete” notation. Past uploads can be viewed at the AWQMS website under the uploader's account.

C - Assessment and Oversight

C-1 - Assessment and Response Actions

Quality Assurance and Quality Control Data will be completed by River Watch staff and requested of all private laboratories. Any data not meeting the standards dictated in the WQCD QAPP will be qualified and flagged or thrown out as deemed necessary. Any data not properly checked for quality assurance by the laboratory will also be qualified in the project's results. If an unacceptable amount of data is being thrown out or flagged, corrective actions will be considered. These will include: switching private laboratories, examining/testing equipment for defects, calibrating equipment between sites vs. once per sampling event, reducing holding times, and retraining of personnel.

C-2 - Reports

After 2017 sampling is completed a full report of the Rifle Creek Investigation will be compiled and distributed to all stakeholders in this watershed. This will include federal land managers, state wildlife / land managers, private landowners, and the City of Rifle.

The purpose of this investigation is to document existing conditions, conduct additional water quality monitoring to better understand pollutant sources and provide a prioritized set of recommendations for implementation of BMPs, both structural and non-structural, to improve water quality. A GIS-based analysis, including field verification, will be performed for inventory and assessment purposes resulting in the creation of a comprehensive geodatabase. Spatial data collection is in progress. Additionally, a reconnaissance-level water quality sampling program will be conducted to isolate sources, both spatial and temporal, of nonpoint source pollution contributions. An interpretation of water quality results superimposed with the geodatabase will guide the initial siting of effective BMPs.

D - Data Validation and Usability

D-1 - Data Review, Validation and Verification

Initial data review will be done by the MCWC sampling leader, Nate Higginson. River Watch staff and private laboratory staff will conduct additional in-depth checking of the data to ensure quality. This data check will be forwarded to the Middle Colorado Watershed Council so that they can make decisions regarding the acceptance and qualifying of data.

D-2 - Validation and Verification Methods

The following steps describe the validation and verification methods that the WQCD Environmental Data Unit uses (and therefore River Watch uses on Middle Colorado Watershed Council data) to verify precision and accuracy. The Middle Colorado Watershed Council will employ these techniques as well.

Unless otherwise specified, acceptable precision for each analytical parameter (e.g., zinc) for a pair of split samples will be < 30%, expressed as relative percent difference (RPD).

$$\text{Precision} = \text{RPD} = \frac{(C - C)}{(C + C)} \times \frac{1}{2} \times 100\%$$

In the event that the difference between split samples is > 30%, data from that site/time will be considered qualified and either deleted or interpreted with caution. Qualified data will be clearly denoted as such in the database.

Estimates of overall precision of a parameter (e.g., zinc) will be derived from the pooled standard deviations (SD) from all individual split pairs. The pooled standard deviation statistic is termed the root mean square and is calculated as:

$$\text{Percent relative standard deviation} = \% \text{RSD} = (\text{SD} / \text{Mean}) \times 100\%$$

$$\text{Root mean square} = \text{RMS} = \frac{\% \text{RSD}^{0.5} + \% \text{RSD}^{0.5} \dots + \text{etc.}^{0.5}}{N}$$

Unless otherwise specified, acceptable RMS for each parameter is < 30%. If RMS is > 30%, then the analysis for that parameter will be deleted from the database or considered as qualified data and interpreted with caution. Qualified data will be clearly denoted in the database.

Concentration of contaminants allowable in field blanks will be project specific. Data from field blanks will be tabulated, reviewed, and interpreted in project reports. If contamination of field blanks occurs, corrective action will be initiated.

The decision process for determining the significance of blank contamination in terms of project and data quality objectives is presented in the following decision criteria:

<u>Field Blank</u>	<u>Reported Analytical Blank</u>	<u>Outcome to Database</u>
--------------------	--------------------------------------	--------------------------------

1. < Detection limit	> detection limit	no change
2. > Detection limit	< detection limit	no change
3. > Detection limit	> detection limit	qualified data (See below)

The decision to accept or reject qualified data will be based on the following criteria:

1. If, after downward adjustment for possible contamination, the analytical values reported for ambient sites still exceed the designated standard (e.g., the stream standard for zinc), then no change in the database is required.
2. If downward adjustment of the ambient site values eliminates exceedance of the designated standards, then the data point(s) are interpreted with caution and re-sampling at the site(s) is appropriate.”

D-3 -- Reconciliation with Data Quality Objectives

All data quality indicators will be calculated at the end of the study. This will include: precision, accuracy, and completeness. If data does not meet the objectives for these indicators the data will be qualified in any reports or discarded. If excessive data is discarded, re-sampling will be considered.

Appendix 1 - References

COLORADO'S SECTION 303(D) LIST OF IMPAIRED WATERS AND MONITORING AND EVALUATION LIST. Colorado Department of Public Health and Environment Water Quality Control Commission. 5 CCR 1002-93 Regulation #93. <https://www.colorado.gov/pacific/cdphe/wqcc-reports-and-plans>. Accessed November 11, 2016.

Quality Assurance Project Plan for Surface Water Monitoring and Assessment. Colorado Department of Public Health and Environment, Water Quality Control Division. May 2015.

Appendix 2 – Field Data Sheets and Chain of Custody Form

MCWC Stream Discharge Data Sheet - Float Method

Station Name _____

Station Number _____ Date ____/____/____

River _____

1. Travel Distance _____ feet

2. Travel Time #1 _____ sec

#2 _____ sec

#3 _____ sec

Avg _____ sec

3. Velocity (distance/time) (v) _____ feet/sec

2. Channel Width @ beginning of segment _____ feet

@ middle of segment _____ feet

@ end of segment _____ feet

Average (w) _____ feet

3. Channel Depth

Location	Depth
1/4 across	
1/2 across	
3/4 across	

Average Depth (d) _____ feet

4. Stream Bottom Type

a. Rough, loose rocks, coarse gravel (0.8)

b. Smooth, mud, sand, hardpan rock (0.9)

(a) _____

Stream Discharge Calculation $Q = v \cdot w \cdot d \cdot a$

Discharge (Q) _____ feet³/sec

Recorded by _____ Date _____

Field Data Sheet

Station Name _____

Station Number _____

River/Stream _____

Date of sample ___/___/___

Volunteer Group _____

Time of sample ___:___

Air T°/Weather/Comments: _____

Sample Collection Method Grab Composite

Samples collected for River Watch analysis: Check all that apply:

<u>Metals</u>	<u>Metals QA/QC</u>	<u>Nutrients</u>	<u>Biological</u>
<input type="checkbox"/> Filtered (F)	<input type="checkbox"/> F Blank	<input type="checkbox"/> TSS/CS	<input type="checkbox"/> Macroinvertebrate
<input type="checkbox"/> Not Filtered (NF)	<input type="checkbox"/> F Duplicate	<input type="checkbox"/> NP Duplicate	<input type="checkbox"/> Macro QA sample
<input type="checkbox"/> No metals	<input type="checkbox"/> NF Blank	<input type="checkbox"/> TSS/CS	<input type="checkbox"/> NP

PARAMETERS

RESULTS

Flow

Gauge Estimate

_____ ft³/second

River Temperature:

_____ Celsius

pH buffer calibration (S.U. = standard unit)

pH 7 \ temperature:

_____ S.U. \ _____ °C

pH 10 \ temperature:

_____ S.U. \ _____ °C

pH sample \ ATC Temp Reading:

(pH \ ATC temp)
_____ S.U. \ _____ °C

Phenolphthalein Alkalinity:

_____ mg/L CaCO₃

Total Alkalinity:

_____ mg/L CaCO₃

Hardness:

_____ mg/L CaCO₃

Dissolved Oxygen:

_____ / mg/L _____ % Saturation

Other:

_____ (unit)

Data recorded by _____

Date recorded _____

Volunteer Time Capture							
Name (use other side if necessary)	Adult or Student	Hours	Mileage	Gas	Equipment	Mailing	Other

- ✓ Enter this data into the River Watch Database at <http://wildlife.state.co.us/riverwatch>
- ✓ Attach all original data sheets to this form and submit to River Watch, keep a copy for your files
- ✓ Record "-0" for all analysis not performed

Hardness Data Sheet

Station Name _____ Station Number _____
River/Stream _____ Date of sample ____/____/____
Volunteer Group _____ Time of sample ____ : ____

TOTAL HARDNESS

1. Amount of sample used (should be 50ml): _____ ml
2. Add ammonia buffer and EBT indicator.
Did solution turn purple? Yes No
3. Titrate from purple to blue.
4. Record the ml of EDTA you added.

end point _____ ml - start point _____ ml = the difference = _____ mL EDTA used

5. Multiply ml of EDTA used by 20 to get the Total Hardness result, and record below.

Example: (7.4 mL EDTA titrant used) x 20 = 148.0 (mg/L) total hardness as CaCO₃

Total hardness _____ (mg/L) CaCO₃

Comments: _____

Data recorded by _____ Date recorded _____

Alkalinity Data Sheet

Station Name _____

Station Number _____

River/Stream _____

Date of sample ___/___/___

Volunteer Group _____

Time of sample ___ : ___

PART I - Phenolphthalein Alkalinity

1. Amount of sample used (should be 50ml): _____ mL

2. pH _____ Is pH greater than 8.3? Yes No

3. Add phenolphthalein indicator. Did solution turn pink? Yes No
If YES → continue with step 4.
If NO → record phenolphthalein alkalinity as 0.0 mg/L, and then go to part II.

4. Titrate from a pink to a clear, record mL of H₂SO₄ you added.

end point _____ mL - start point _____ mL = the difference = _____ mL H₂SO₄ used

5. Multiply mL of H₂SO₄ used by 40. Record this as the phenolphthalein alkalinity.

Example: 0.2 ml H₂SO₄ titrant used x 40 = 8.0 mg/L CaCO₃

Phenolphthalein Alkalinity Result _____ mg/L CaCO₃

(Note: If you have phenolphthalein alkalinity, DO NOT rezero the buret before continuing.)

PART II - Total Alkalinity

6. Add BGMR indicator. Did solution turn blue? Yes No

7. Titrate from turquoise to pink-gray. Record mL of H₂SO₄ added.

_____ mL H₂SO₄ used

8. Multiply mL of H₂SO₄ used by 20. This is the total alkalinity.

Example: (2.5 mL H₂SO₄ titrant used) x 20 = 50.0 mg/L

Total Alkalinity result _____ mg/L CaCO₃

Comments: _____

Data Recorded by: _____

Date: _____

Dissolved Oxygen Data Sheet

Station Name _____

Station Number _____

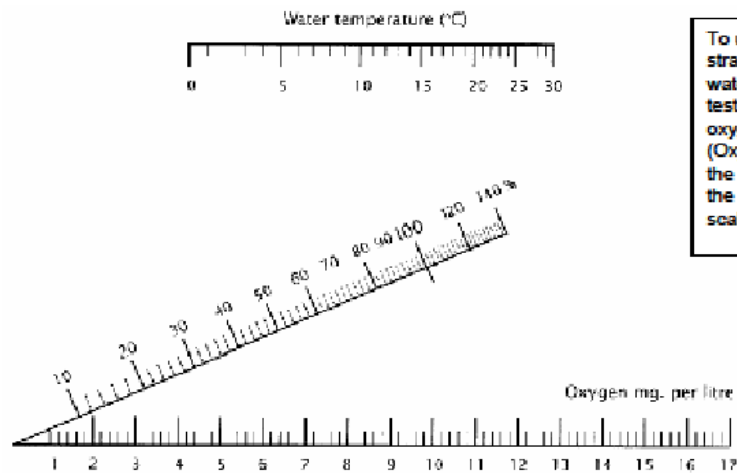
River/Stream _____

Date of sample ___/___/___

Volunteer Group _____

Time of sample ___:___

1. River temperature _____ ° Celsius
2. Titrate start point _____ ml
3. Titrate end point _____ ml
4. Subtract starting point from end point: # of ml at start point - # of ml at end point = milliliters of titrant used
 milliliters of titrant used = mg/L dissolved oxygen _____ mg/L
5. Determine the percent saturation of dissolved oxygen using the chart below.



To use the chart, draw a straight line between the water temperature at the test site and the dissolved oxygen measurement (Oxygen mg/L), and read the saturation percentage at the intercept on the sloping scale.

Percent Saturation _____ %

Comments: _____

Data recorded by _____

Date recorded _____

Chain of Custody

Volunteer Group _____

Date Shipped ____ / ____ / ____

Shipped by _____

Signature _____

Field Data Sheets included - Yes No Field Data entered via web - Yes No

Station Name	Station Number	Date	Time	Metal Samples	Nutrients	Macroinvertebrate Sample	
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____
				Filtered (F) _____ F Blank _____ F Duplicate _____	Non-Filtered(NF) _____ NF Blank _____ NF Duplicate _____	TSS / CS NP Duplicate TSS / CS NP	Yes QA sample _____

F = filtered NF= non-filtered FB = filtered blank NFB = non- filtered blank FD = filtered duplicate NFD = non-filtered duplicate
 Nutrients unpreserved (32 ounce jug): TSS = total suspended solids and CS = Chloride, Sulfate
 Nutrients preserved with H₂SO₄ (8 ounce cylinder): NP = Nitrate + Nitrite, Ammonia, Total Phosphorous

Total number of metals bottles in cooler _____

Total number of nutrient bottles _____

Total number of macroinvertebrate samples _____

Ship samples to River Watch, 6060 Broadway, Denver Colorado 80216.

River Watch Staff Section

Total number of metals bottles received _____

Date Samples Received _____

Total number of nutrient bottles received _____

Received by _____