

# PURGATOIRE RIVER WATERSHED MONITORING NETWORK

## 2010 SAMPLING ANALYSIS PLAN

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Developed for

The Consortium of Coalbed Methane Operators in the  
Raton Basin of the Purgatoire River

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## **1.0 PURGATOIRE RIVER WATER QUALITY MONITORING PROGRAM OVERVIEW**

### **1.1 Introduction**

This Sampling Analysis Plan (SAP) shall serve as support for field work performed by Tetra Tech, Inc. in the Purgatoire River Basin (the “basin”), during the duration of the water quality monitoring program. This SAP will provide guidance for field personnel by defining, in detail, the number, type, and location of samples to be collected; and the type of analyses to be performed. This SAP follows the general guidelines for development of field sampling plans presented in U.S. EPA (1988).

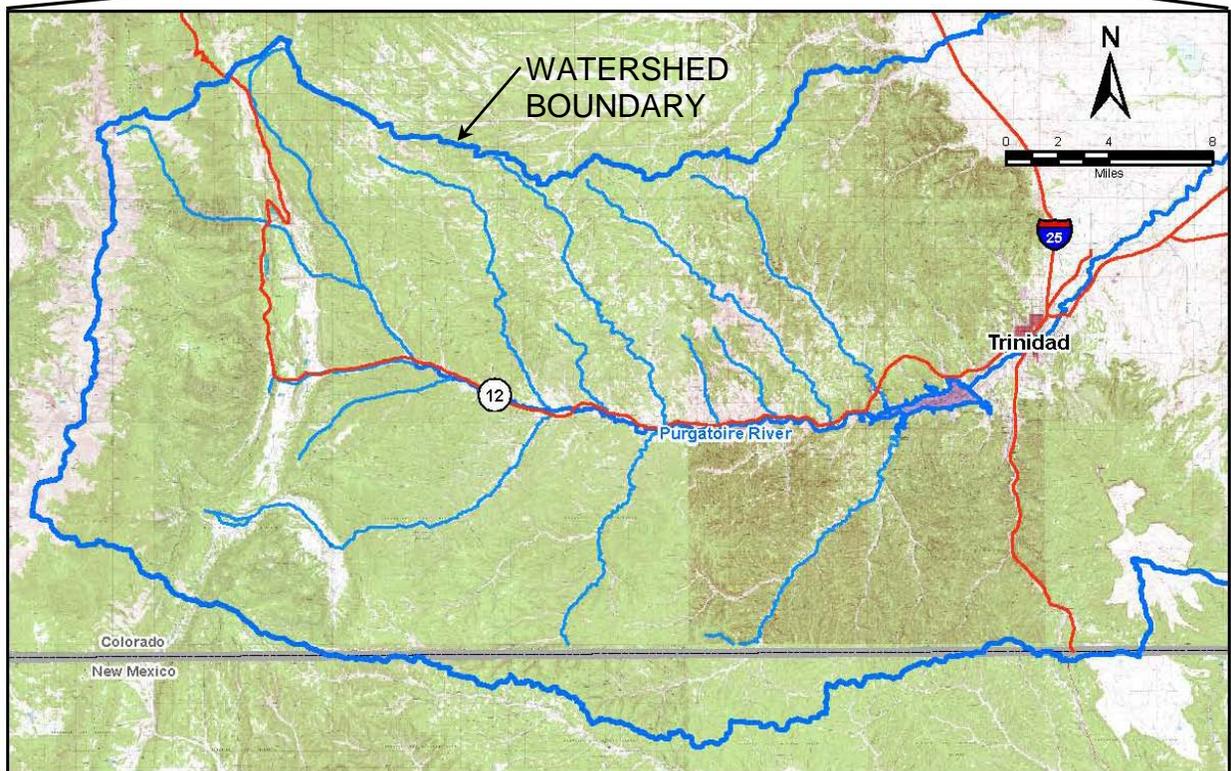
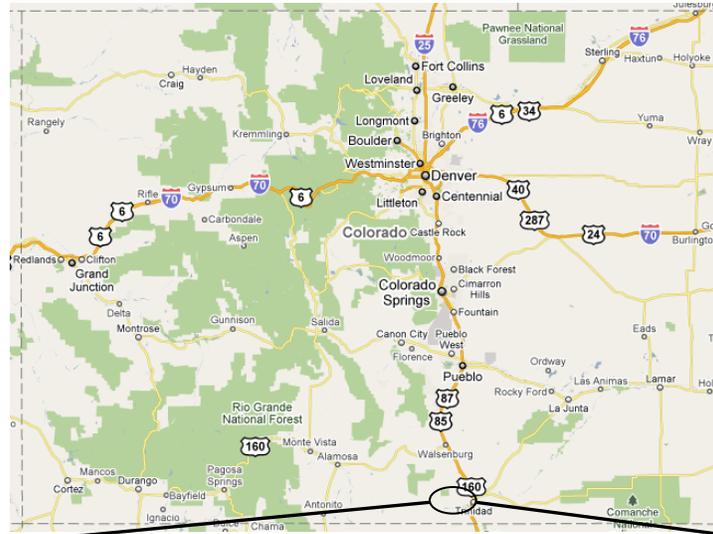
This SAP was developed for the use of Tetra Tech, Inc. and approved Tetra Tech, Inc. contractors. Tetra Tech, Inc. will provide the majority of the technical and field staff to perform the sampling and reporting aspects of the individual projects related to this work. Qualified subcontractors will perform the following specific tasks:

- ACZ Laboratories, Inc., Steamboat Springs, CO – to provide sample analysis.
- Sutron Corporation, Sterling, VA – to provide satellite telemetry and web hosting services for real-time gage station data.

### **1.2 Project Background**

The study area of the Purgatoire River Basin (the “basin”) is west of the Town of Trinidad, Colorado in Las Animas County. The basin covers approximately 400 square miles located between Interstate 25 and the Sangre de Cristo mountain range. A vicinity map is shown in Figure 1.

Currently, the Coal Bed Methane (CBM) operators in this watershed have approximately 3,500 CBM extraction wells with approximately 10 MGD of produced water discharged in the basin. The water quality of produced water is not fully understood in this region, including constituents such as sodium, calcium, magnesium, specific conductance, boron, selenium, iron, as well as Sodium Adsorption Ratio (SAR). Currently, discharge permit requirements are largely influenced by agricultural uses that may be impacted from elevated levels of constituents found in produced water (e.g., sodium, total dissolved solids, magnesium, and calcium, etc.). Implementation of this watershed monitoring program will provide important data and information to understand geochemical influences and characterize water quality in the Purgatoire River and select tributaries potentially influenced by the CBM operations. It also provides satellite monitoring of near-real time data to landowners, agencies, and stakeholders, supporting an approach of transparent communication of data to entities interested in this information.



**Figure 1 Purgatoire River Watershed Vicinity Map**

The Purgatoire River watershed monitoring program includes 27 locations on the Purgatoire River and associated tributaries (Figure 2). Ten sample locations are on the mainstem or Middle Fork of the Purgatoire River while seventeen locations are on tributaries to the Purgatoire River. The basis for each of these sampling locations is summarized in Table 1. Seven of the twenty-seven monitoring locations will have continuous gaging stations to monitor flow and/or water quality. Monitoring equipment

will measure streamflow, pH, specific conductance, temperature, and chloride at 15-minute intervals.

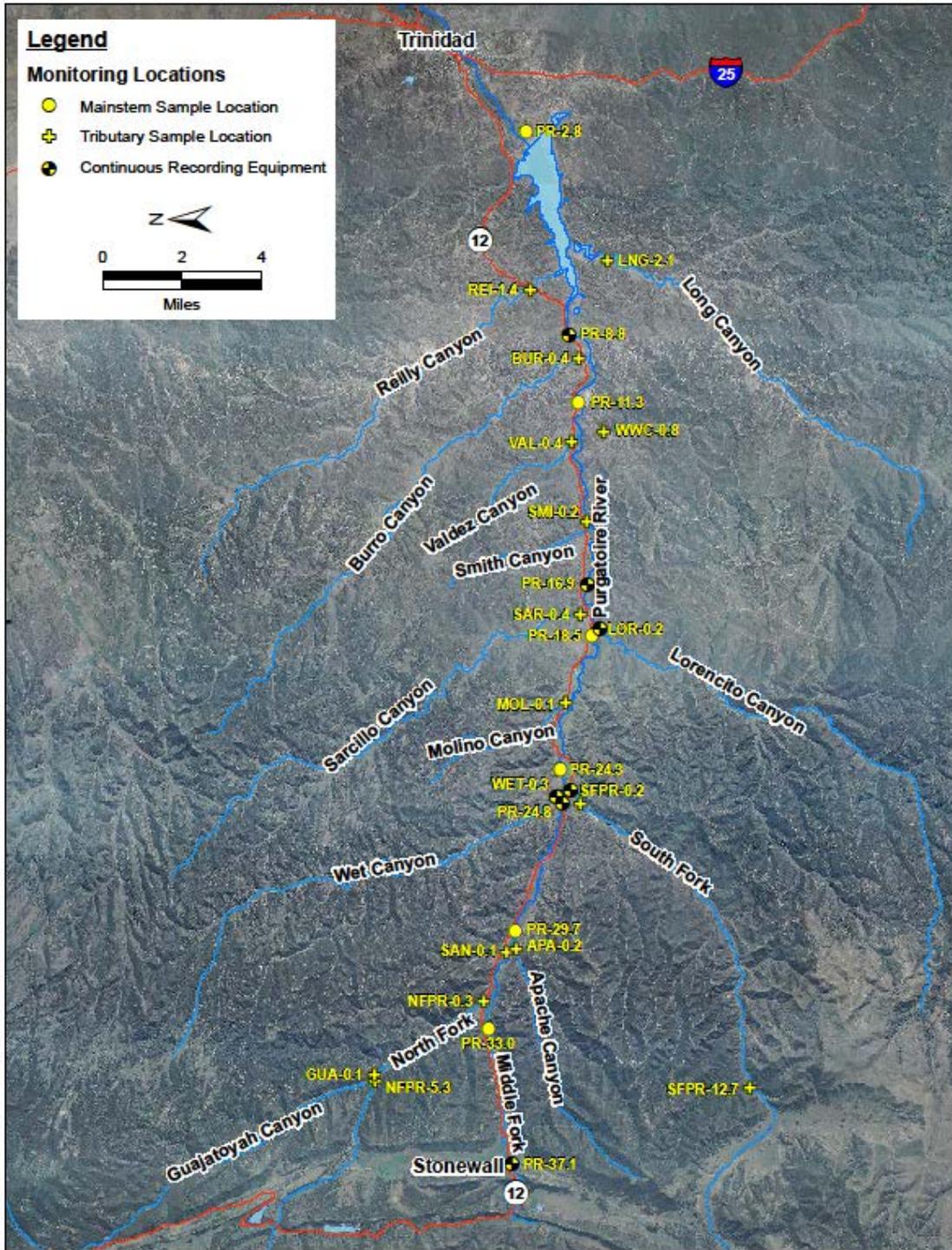


Figure 2 Sampling Locations

**Table 1 Sampling Locations**

**SURFACE WATER MONITORING LOCATIONS  
PURGATOIRE RIVER BASIN SITE-WIDE MONITORING PROGRAM**

Sample Identification	Mainstem Location	Tributary Location	Reasoning for Sample Location	Influenced by CBM Discharge	Continuous Streamflow Monitoring Equipment <sup>1</sup>	Water Quality Monitoring Equipment <sup>2</sup>	Routine Monitoring
PR-37.1	Middle Fork Purgatoire River at Stonewall		Provide background flow and water chemistry for the Middle Fork Purgatoire River. Supplement historic data.	No	X	X	X
PR-33.0	Middle Fork Purgatoire River u/s North Fork Purgatoire River		Evaluate flow and water chemistry influences (e.g., New Elk Mine, CBM production) on the Middle Fork Purgatoire River between Stonewall and the North Fork Purgatoire River.	Yes			X
NFPR-5.3		North Fork Purgatoire River u/s Guajatoyah Creek	Provide background flow and water chemistry for the North Fork Purgatoire River. Supplement historic data.	No			X
GUA-0.1		Guajatoyah Creek u/s North Fork Purgatoire River	Guajatoyah Canyon flow and water chemistry contributions to the North Fork Purgatoire River. Supplement historic data.	Yes			X
NFPR-0.3		North Fork Purgatoire River at Hwy 12 Bridge	Evaluate flow and water chemistry influences to the mainstem Purgatoire River from the North Fork Purgatoire River. Supplement historic data.	Yes			X
SAN-0.1		Sanistevan Canyon near Mouth	Evaluate flow, water chemistry, and water quality influences to the Middle Fork Purgatoire River from Sanistevan Canyon.	Yes			X
APA-0.2		Apache Canyon near Mouth	Evaluate flow, water chemistry, and water quality influences to the Middle Fork Purgatoire River from Apache Canyon.	Yes			X
PR-29.7	Middle Fork Purgatoire River d/s Apache Canyon		Evaluate flow and water chemistry in the Middle Fork Purgatoire River between the North Fork Purgatoire River and Wet Canyon. Supplement historic data.	Yes			X
PR-24.8	Middle Fork Purgatoire River u/s Wet Canyon		Evaluate flow, water chemistry, and water quality in the mainstem Purgatoire River between the North Fork Purgatoire River and Wet Canyon.	Yes	X	X	X
WET-0.3		Wet Canyon near Mouth	Evaluate flow, water chemistry, and water quality influences to the Middle Fork Purgatoire River from Wet Canyon. Elevated loading of select permit constituents.	Yes	X	X	X
SFPR-12.7		South Fork Purgatoire River d/s of Tercio, CO	Provide background flow and water chemistry for the South Fork Purgatoire River. Supplement historic data.	No			X
SFPR-0.2		South Fork Purgatoire River near Mouth	Evaluate flow, water chemistry, and water quality influences on the mainstem Purgatoire River from the South Fork Purgatoire River. Elevated loading of select permit constituents.	Yes	X	X	X
PR-24.3	Mainstem Purgatoire River d/s South Fork Purgatoire River and Wet Canyon		Isolate "upper basin" from "lower basin" influences. Evaluate flow and water chemistry for the mainstem Purgatoire River d/s of Wet Canyon and South Fork Purgatoire River influences. Provide comparison to PR-24.8.	Yes			X
MOL-0.1		Molino Canyon at Hwy 12	Evaluate flow and water chemistry influences on the mainstem Purgatoire River from Molino Canyon.	No			X
PR-18.5	Purgatoire River at Lorencito Canyon Bridge		Evaluate flow and water chemistry on the mainstem Purgatoire River prior to Lorencito Canyon and Sarcillo Canyon influences. Supplement historic data.	Yes			X
LOR-0.2		Lorencito Canyon near Mouth	Evaluate flow, water chemistry, and water quality influences to the mainstem Purgatoire River from Lorencito Canyon. Elevated loading of select permit constituents.	Yes	X	X	X
SAR-0.4		Sarcillo Canyon near Mouth	Evaluate flow, water chemistry, and water quality influences to the mainstem Purgatoire River from Sarcillo Canyon. Elevated loading of select permit constituents.	Yes			X
PR-16.9	Purgatoire River below Sarcillo Canyon		Evaluate flow, water chemistry, and water quality in the mainstem Purgatoire River d/s of Lorencito Canyon and Sarcillo Canyon influences.	Yes	X	X	X

Sample Identification	Mainstem Location	Tributary Location	Reasoning for Sample Location	Influenced by CBM Discharge	Continuous Streamflow Monitoring Equipment <sup>1</sup>	Water Quality Monitoring Equipment <sup>2</sup>	Routine Monitoring
SMI-0.2		Smith Canyon at Hwy 12	Evaluate flow and water chemistry influences to the mainstem Purgatoire River from Smith Canyon. Supplement historic data.	Yes			X
VAL-0.4		Valdez Canyon at Hwy 12	Evaluate flow and water chemistry influences to the mainstem Purgatoire River from Valdez Canyon.	Yes			X
WWC-0.8		Widow Woman Canyon near Mouth	Evaluate flow and water chemistry influences to the mainstem Purgatoire River from Widow Woman Canyon. Supplement historic data.	No			X
PR-11.3	Purgatoire River at Pioneer Entrance Bridge		Evaluate flow and water chemistry on the mainstem Purgatoire River upstream of Burro Canyon. Supplement historic data.	Yes			X
BUR-0.4		Burro Canyon at Hwy 12	Evaluate flow and water chemistry influences to the mainstem Purgatoire River from Burro Canyon.	Yes			X
PR-8.8	Purgatoire River at Long Canyon Bridge		Provide basin-wide flow, water chemistry, and water quality (excluding influences from Reilly and Long Canyon) to evaluate influences from CBM production on the Purgatoire River u/s Trinidad Lake. Supplement historic data.	Yes	See Notes <sup>3</sup>	X	X
REI-1.4		Reilly Canyon near Mouth	Evaluate flow, water chemistry, and water quality influences to the mainstem Purgatoire River/Trinidad Lake from Reilly Canyon. Elevated loading of select permit constituents.	Yes			X
LNG-2.1		Long Canyon near Mouth	Evaluate flow and water chemistry influences to the mainstem Purgatoire River/Trinidad Lake from Long Canyon. Supplement historic data.	No <sup>4</sup>			X
PR-2.8	Purgatoire River below Trinidad Lake		Provide flow and water chemistry data downstream of Trinidad Lake to evaluate basin-wide influences from CBM production. Provide comparison to PR-8.8 to evaluate water chemistry changes through the lake.	Yes	See Notes <sup>5</sup>		X

Notes:

=Tributary Location

u/s = Upstream

d/s = Downstream

1 = Continuous Streamflow Monitoring Equipment, Monitors streamflow at set intervals (e.g., 15-minutes).

2 = Continuous Water Quality Monitoring Equipment, Hydrolab water quality (i.e., pH, temperature, specific conductivity, chloride) equipment to record at set intervals (e.g., 15-minutes).

3 = Flow data provided from existing USGS gaging station at Long Canyon bridge (Station ID: Purgatoire River at Madrid, CO 07124200).

4 = Produced water from Pioneer Long Canyon CBM operations is re-injected.

5 = Flow data provided from existing USGS gaging station below Trinidad Lake (Station ID: Purgatoire River below Trinidad Lake, CO 07124410).

### 1.3 Project Description

This SAP covers work under the following two tasks to be performed beginning March 2010.

1. Monthly Monitoring
2. Continuous Monitoring

The scopes of these monitoring programs are described in the subsequent sections.

#### 1.3.1 *Monthly Monitoring Program*

The Purgatoire River watershed monitoring program will incorporate 27 sample locations as outlined in Table 1. Sample locations are selected to:

- Provide background surface water quality and flow data in the South, Middle, and North Forks of the Purgatoire River prior to CBM discharge influences.
- Evaluate changes in water chemistry and flow along the mainstem of the Purgatoire River from above CBM influences to below Trinidad Lake, where agricultural diversions generally occur.
- Provide surface water chemistry and flow data in tributaries influenced by CBM operations to evaluate their impact on the Purgatoire River.
- Provide surface water data that supplements historic sampling data, where available.
- Provide the optimal location for continuous flow and water quality monitoring equipment to support project objectives.

Monthly surface water monitoring will utilize two field teams responsible for sample collection and streamflow measurement. Sampling will be performed to evaluate chemistry and load changes in the Basin's surface water. Monthly monitoring will allow the evaluation of seasonal water quality trends within the Basin. For example, the May/June monitoring events will target seasonal snowmelt runoff when the ratio of CBM produced water to Purgatoire River flows are generally lowest. Alternatively, the December through February monitoring events will target seasonal baseflows when the ratio of CBM produced water to Purgatoire River flows are generally highest.

The monthly sampling will likely be performed over a two-day period due to the size of the Purgatoire River basin. Sampling will be conducted in a downstream fashion from the uppermost sample station at Stonewall (PR-37.1) to below Trinidad Lake (PR-2.8). Although sampling will be performed in a downstream fashion, adherence to surface water travel times between stations (i.e., synoptic sampling<sup>1</sup>) will not be followed due to the relative size of the Basin. Efforts will be made to collect samples from all Purgatoire

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<sup>1</sup> Synoptic sampling is the sampling of a slug or parcel of water as it moves downstream past a specified station. Generally, travel times between monitoring stations are measured prior to collecting samples.

River mainstem surface water stations (i.e., “PR” suffix) on the same day to promote data capability. If multiple days are required, a sample will be collected on the second day at a location where sampling ended on the first day. This duplication in sampling will allow a correlation between the water quality and flow characteristics over the two-day sampling period.

In accordance with standard water quality protocol, each team will collect field duplicate and equipment rinsate blank samples for QA/QC purposes during each event. Sampling teams will collect field measurements (i.e., pH, temperature, and specific conductance) at each sample location. Surface water samples will be collected and placed in sample bottles provided by the laboratory. Sample aliquots collected for dissolved analyses will be field filtered using a 0.45-micron filter. Upon collection, the samples will be placed in a chilled cooler for shipment under chain-of-custody procedures to ACZ Laboratories, Inc. for analytical testing. The analytical suite for each sample incorporates the analyses presented in Tables 2a and 2b.

**Table 2a Routine Sampling Parameters**

	<b>Constituent</b>	<b>U.S. EPA Method Number</b>	<b>Sample Preservation and Treatment</b>	<b>Holding Times</b>
Field Parameters	pH	150.1	Measure In-Situ	Immediately
	Specific Conductance	120.1		28 days
	Temperature	170.1		Immediately
Metals	Boron <sup>D,T</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Calcium <sup>D</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Iron <sup>D,TR</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Magnesium <sup>D</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Potassium <sup>D</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Sodium <sup>D</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
Wet Chemistry	Alkalinity	SM2320B - Titration	Chill to 4 degrees C	14 days
	Chloride	SM4500	Chill to 4 degrees C	28 days
	Sodium Adsorption Ratio	USGS – I1738-78	Calculation	---
	Sulfate	375.3 Gravimetric	Chill to 4 degrees C	28 days
	Total Suspended Solids (TSS)	160.2 Gravimetric	Chill to 4 degrees C	7 days
	Total Dissolved Solids (TDS)	160.2 Gravimetric	Chill to 4 degrees C	7 days

**NOTES:**

1. D = Dissolved form analysis.
2. T = Total form analysis.
3. TR = Total recoverable form analysis.
4. Filtration performed in the field at the time of sample collection.
5. Sodium Adsorption Ratio (SAR) calculated based on dissolved calcium, magnesium, and sodium concentrations.
6. Routine parameters tentatively represent January, March, April, May, July, September, October, and December.

**Table 2b Quarterly Sampling Parameters**

	<b>Constituent</b>	<b>U.S. EPA Method Number</b>	<b>Sample Preservation and Treatment</b>	<b>Holding Times</b>
Field Parameters	pH	150.1	Measure In-Situ	Immediately
	Specific Conductance	120.1		28 days
	Temperature	170.1		Immediately
Metals	Boron <sup>D,1</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Calcium <sup>D,1*</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Copper <sup>D,TR</sup>	200.8 ICP-MS	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Iron <sup>D,TR</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Lead <sup>D,TR</sup>	200.8 ICP-MS	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Magnesium <sup>D,1*</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Potassium <sup>D</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Selenium <sup>D,TR</sup>	200.8 ICP-MS	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Sodium <sup>D,1*</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
	Zinc <sup>D,TR</sup>	200.7 ICP	Acidify with HNO <sub>3</sub> ; pH <2	6 months
Wet Chemistry	Alkalinity	SM2320B - Titration	Chill to 4 degrees C	14 days
	Chloride	SM4500	Chill to 4 degrees C	28 days
	Sodium Adsorption Ratio	USGS – I1738-78	Calculation	---
	Sulfate	375.3 Gravimetric	Chill to 4 degrees C	28 days
	Total Suspended Solids (TSS)	160.2 Gravimetric	Chill to 4 degrees C	7 days
	Total Dissolved Solids (TDS)	160.2 Gravimetric	Chill to 4 degrees C	7 days

**NOTES:**

1. D = Dissolved form analysis.
2. T = Total form analysis.
3. TR = Total recoverable form analysis.
4. Filtration performed in the field at the time of sample collection.
5. Sodium Adsorption Ratio (SAR) calculated based on dissolved calcium, magnesium, and sodium concentrations.
6. Quarterly parameters tentatively represent February, June, August, and November.
7. \* = Total analyses for calcium, magnesium, and sodium performed only at Stations PR-24.8, PR-16.9, and PR-8.8 for SAR calculations.

Stream discharge will be measured at each sample location using portable cutthroat flumes or the equal-width-increment method (ASTM Standard D3858-95) for flows greater than 0.5 cubic feet per second (cfs).

**1.3.2 Continuous Monitoring Program**

Seven of the twenty-five sites identified in Table 1 will be continuous monitoring sites as well as monthly monitoring sites. The main focus of operating and maintaining continuous flow and water quality monitoring stations is to assess the hydrological and geochemical conditions of the Purgatoire River and select tributaries during time periods other than when monthly surface water sampling events occur. Another important feature regarding continuous monitoring is evaluating long-term (seasonal) and short-

term (storm events) flow and water quality changes in the Purgatoire River and select tributaries.

Seven<sup>2</sup> gaging stations with continuous flow and/or water quality monitoring equipment are located at select Purgatoire River and tributary stations. Sample location PR-8.8 (upstream of Trinidad Lake) is the only station that will not incorporate flow monitoring equipment because the USGS currently maintains a streamflow gage at this location<sup>3</sup>.

Gage stations will incorporate a Sutron Accubar constant flow bubbler-type pressure gage that measures the depth of streamflow and converts the depth to an appropriate discharge. Continuous water quality (i.e., pH, temperature, specific conductivity, and chloride) monitoring will utilize a Hach DS-5 Multiprobe<sup>4</sup>. Data measured by flow and water quality equipment will be stored on Sutron 9210 data collection platforms (DCP) at 15-minute intervals.

The DCP, bubbler-type gage, and other associated equipment will be housed in a metal gage enclosure to protect from weather and vandalism. A polyvinyl chloride (PVC) enclosure will be constructed around the water quality probe and cable to help protect from weather and vandalism.

Satellite transmission of the near-real time gaging station data will be via the Iridium satellite, contracted through Sutron Corporation. The flow and water quality data will be transmitted to satellite links by each DCP at set intervals (e.g., 1-hour intervals). Data will then be available for viewing via a world-wide-web site operated by Sutron Corporation.

Operation and maintenance of the flow and water quality monitoring equipment includes programming and setup of DCPs, Hach multi-probes, and bubbler-type gages, weekly cleaning and monthly calibrating of the water quality probes and bubbler-type gages, replacement of chloride probe sensors every five months (Station PR-37.1 only), and rating curve development.

## **2.0 MONITORING PROGRAM MANAGEMENT**

### **2.1 Project/Task Organization**

The project and task organization for the Purgatoire River Watershed Monitoring program is shown in Figure 3. The roles and responsibilities of each of the organizations identified in Figure 3 are summarized in sections 2.2 through 2.9.

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<sup>2</sup> The Sarcillo Canyon (SAR-0.4) and Reilly Canyon (REI-1.4) gaging stations were decommissioned during the summer of 2013 due to flood damage.

<sup>3</sup> USGS gaging station at Long Canyon Bridge (Station ID: Purgatoire River at Madrid, CO 07124200)

<sup>4</sup> Chloride at all stations except PR-37.1 will be calculated based on chloride vs specific conductivity relationships developed for each station. PR-37.1 currently includes a water quality probe to measure in-situ chloride.



**Figure 3 Project Organization**

Note: TT = Tetra Tech, Inc.

## **2.2 CBM Consortium**

The CBM Consortium consists of representatives from the two CBM companies in the Purgatoire River watershed, namely, Pioneer Natural Resources and XTO Energy. The CBM Consortium has the ultimate responsibility for providing leadership and direction on this watershed water-quality monitoring program. The CBM Consortium has contracted with Tetra Tech, Inc. to implement and maintain the water quality monitoring program. The program will be conducted in coordination with state agencies and in accordance with this SAP.

## **2.3 Project Manager**

Ms. Julie Vlier, P.E. is project manager for this monitoring program. Ms. Vlier manages the project, directs staff, and reviews all technical matters for the project including review of the water-quality monitoring program and QA/QC tasks. The Project Manager is responsible for the review and approval of this SAP and other monitoring program documents and project communication.

## **2.4 Program Administrator**

The Program Administrator, Marshall Massaro, is responsible for overseeing the performance of the water-quality monitoring program and ensures that the program is

conducted in accordance with all requirements. He is responsible for the implementation of this SAP and the water-quality monitoring program and staffs the program with the appropriate number of qualified and trained staff and performs oversight of field teams. The Administrator reviews field data sheets, verification/validation of analytical data, maintenance of the program database, and all required reporting. The Project Manager performs required quality assurance and quality control duties.

## **2.5 QA/QC Manager**

The QA/QC manager implements QA/QC protocol, reviews QA/QC tasks, and provides oversight and guidance on the overarching QA/QC program.

## **2.6 Data Manager**

The data manager downloads data and information into databases for evaluation, analysis, and reporting using ARC-Info and MS Access software.

## **2.7 Field Team Leaders**

The Field Leader appoints trained and qualified field teams to perform monitoring activities. The Field Leader schedules laboratory and other required services and reviews and approves all field data sheets prior to transmittal to the Project Manager.

## **2.8 Field Team Technicians**

The field technicians are responsible for conducting all field activities in accordance with this SAP, QA/QC protocols, and Health and Safety Plan procedures adopted by Tetra Tech, Inc.

## **2.9 Subcontracted Analytical Laboratories**

ACZ Laboratories, Inc. will perform all analyses requested by the Project Manager in accordance with established procedures and approved quality assurance plans.

## **3.0 MONITORING OBJECTIVES AND DATA EVALUATION**

The objectives of the watershed monitoring program are:

1. Provide water quality data to more fully understand and evaluate CBM influences on surface water quality and loading to tributaries and ultimately, the Purgatoire River both upstream and downstream of Trinidad Lake.
2. Provide continued hydrologic and surface water quality data for the evaluation of the upper Purgatoire River and associated tributaries throughout various flow regimes.

3. Evaluate pollutant loads, trends in the concentrations, and assimilative capacity to develop management scenarios, creative options and control strategies to achieve permit compliance.
4. Allow a comprehensive, site-wide comparison of water quality constituents of concern to applicable permit limits and WQCC water quality standards.
5. Understand sodium adsorption ratio (SAR) and electrical conductivity (EC) relationship in the watershed as it relates to irrigated agriculture and classified uses.
6. Provide a scientific and technical basis to support permitting and water management options.

### **3.1 Evaluation of Data**

Data obtained throughout the monitoring program (i.e., analytical data, manual flow and water quality data) will be maintained by Tetra Tech, Inc. in a Microsoft Access database. Prior to importing data into the database, a data usability assessment will be conducted on water chemistry data to ensure proper data quality. Tetra Tech, Inc. will evaluate the surface water monitoring results following each calendar year of monitoring and provide a data summary/evaluation report to each member of the CBM consortium. The report will include a summary of continuous flow and water quality data collected during the year as part of this surface water monitoring program. The summary report will include tabular and graphical representations of collected data and an evaluation of the data including noticeable chemistry and loading trends and how they compare to permit limits.

In addition to the routine compilation and presentation of the monitoring data collected, Tetra Tech, Inc. will perform more extensive evaluation of the data. Examples of the data evaluations include:

1. Perform time-trend and spatial analyses on select monitoring data.
2. Evaluate historical data.
3. Verify and validate data, and conduct statistical evaluation for outliers.

### 3.2 Data Quality Objectives

The project objective is to collect data that complies with WQCD rules for surface-water quality monitoring programs, to support decisions related to stream standards modifications, permit decisions, and water quality assessments. The following paragraphs define the measurement performance criteria necessary to support the project objective.

Accuracy and precision are crucial aspects of analytical data and this monitoring program. Accuracy is defined as “the degree of agreement of a measured value with the true or expected value.” Laboratory accuracy is measured in percent recoveries (PR). Precision is “the degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions.” In other words, precision is the relative size of a group of shots on a target. Laboratory precision is measured in Relative Percent Difference (RPD). PR and RPD are measured and reported by labs for every individual analysis. Table 3 illustrates the precision and accuracy for the Purgatoire Watershed field and laboratory analyses. These values represent worst cases estimates. The data collection precision and accuracy measurements are well within these estimates.

**Table 3 Data Precision and Accuracy Estimates**

Matrix	Parameter	Precision	Accuracy
Water	pH	± 0.05	0.01 s.u.
Water	Specific Conductance	± 1%	0.01 mS/cm
Water	Temperature	± 0.3	0.1 C
Water	Boron (Dissolved)	± 20%	80-120
Water	Calcium (Dissolved)	± 20%	80-120
Water	Calcium (Total)	± 20%	80-120
Water	Copper (Dissolved)	± 20%	80-120
Water	Copper (Total Recoverable)	± 20%	80-120
Water	Iron (Dissolved)	± 20%	80-120
Water	Iron (Total Recoverable)	± 20%	80-120
Water	Lead (Dissolved)	± 20%	80-120
Water	Lead (Total Recoverable)	± 20%	80-120
Water	Magnesium (Dissolved)	± 20%	80-120
Water	Magnesium (Total)	± 20%	80-120
Water	Selenium (Dissolved)	± 20%	80-120
Water	Selenium (Total Recoverable)	± 20%	80-120
Water	Sodium (Dissolved)	± 20%	80-120
Water	Sodium (Total)	± 20%	80-120
Water	Zinc (Dissolved)	± 20%	80-120
Water	Zinc (Total Recoverable)	± 20%	80-120
Water	Alkalinity	± 20%	80-120
Water	Chloride	± 20%	80-120
Water	Sulfate	± 20%	80-120
Water	Total Suspended Solids	± 20%	80-120
Water	Total Dissolved Solids	± 20%	80-120

### **3.3 Measurement Performance Criteria**

The usability of the field and laboratory analytical data will be established through an evaluation of the precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters. The evaluation procedure utilizes the guidelines presented in the U.S.EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (U.S. EPA, 2010) and in specific analytical methods used for the assessment of data usability.

## **4.0 MEASUREMENT AND DATA ACQUISITION**

This section presents a description of field activities to be conducted during the monthly and continuous monitoring programs. Field methods, sampling procedures, and QA/QC protocols are presented.

### **4.1 Sampling Location and Frequency**

Table 1 and Figure 1 present sample locations and sampling frequency.

### **4.2 Basic Monitoring Program**

The basic monitoring program parameters are provided in Tables 2a and 2b, and the rationale for the selection of these parameters is provided in Section 4.3.

### **4.3 Parameter Rationale**

The monitoring parameters for this program were selected to maximize the use of available financial resources while still meeting the objectives of the program. The rationale for the selection of the monitoring parameters is summarized below.

#### ***4.3.1 Field Parameters***

All aqueous surface water samples will be tested in the field for pH, specific conductivity, and temperature per the methods specified in Tables 2a and 2b. Additionally, streamflow will be measured at each sample location during throughout the water quality monitoring program. These field parameters will aid in the evaluation of overall water quality and provide additional data regarding source areas for monitored constituents. Streamflow measurements will allow an evaluation of constituent loads entering the Purgatoire River surface water system.

#### ***4.3.2 Metals Analyses***

Each sample collected as part of the watershed monitoring program will be analyzed for the metals identified in Tables 2a and 2b. Metal constituents will be analyzed for total, total recoverable, and/or dissolved forms. Specific metal forms scheduled for analysis

were selected based on current CBM surface water discharge permit limits as well as select forms presented in the *WQCC Classifications and Numeric Standards for the Arkansas River Basin* (Effective March 30, 2009).

#### 4.3.3 *Wet Chemistry Analyses*

Similar to metals analyses, the wet chemistry analyses provided in Tables 2a and 2b were selected based on current CBM surface water discharge permit limits as well as select constituents regulated by the WQCC through “*The Basic Standards and Methodologies for Surface Waters (Regulation No.31)*” and “*The Classifications and Numeric Standards for the Arkansas River Basin, (Regulation No. 32)*”, as well as WQCD Policy No. WQP-24, “*Implementing Narrative Standards in Discharge Permits for the Protection of Irrigated Crops.*” Specifically, electrical conductivity, sodium concentration, and Sodium Adsorption Ratio (SAR) (which is representative of the relative proportion of sodium cations to calcium, and magnesium cations) can inhibit the agricultural use of surface water if concentrations exceed specified stream standards.

## 5.0 **SAMPLE DESIGNATION, HANDLING AND ANALYTICAL TESTING METHODS**

### 5.1 **Sample Designation**

Water samples will be labeled using their location/site identification and the date of collection. The sample location name is to be followed by a hyphen and the date in six-digit format (MMDDYY). For example, a surface water sample collected from the Purgatoire River at Station PR-8.8 on May 15, 2010 would be identified as PR8.8-051510 on the sample label.

Field duplicate samples will be designated with a “D” after the sample date (e.g., PR8.8-051510D). Equipment rinse samples will be designated with an “ERB” as the sample location, followed by the team number (i.e., Team 1 or Team 2), followed by the date as described previously (e.g., ERB1-051510). Team 1 represents the team sampling the mainstem stations and Team 2 represents the team sampling the tributary stations.

### 5.2 **Sample Handling Procedures**

Sampling procedures will be conducted in a manner which assures that samples and field data are representative, and that the resultant data can be duplicated for comparison to subsequent data sets. These sample handling procedures will be followed to ensure the integrity of the samples during collection, transportation, analysis, and reporting. The protocols outlined below present minimum handling procedures for surface water sampling. All documentation will be completed using permanent markers.

Analytical aqueous samples will be filtered in the field at the time of collection and placed in new sample containers obtained from the laboratory. The laboratory will have “pre-charged” the sample containers with preservatives (e.g., HNO<sub>3</sub>, etc.), as

appropriate. The sample containers will be labeled in the field with the following information:

- Company name (Tetra Tech, Inc.).
- Sample identification (see Section 5.1).
- Sample date and time (military time or 24-hour clock).
- Preservative type.
- Sample type (i.e., raw or unfiltered water, filtered water).

All samples transmitted to the laboratory will be accompanied by a Chain-of-Custody Record form. The following information will be supplied in the indicated spaces to complete the Chain-of-Custody Record form:

- Tetra Tech's name and address in the "Report to" and "Invoice to" section
- Project (job) number.
- Shipping method and tracking number.
- Sample identification.
- Sample date and time.
- The sample matrix (i.e., "SW" for surface water).
- The number of containers (aliquots) associated with the specific sample.
- The analyses to be performed on the specific sample.
- Remarks, as needed.
- Signatures of individuals relinquishing possession of the samples in the designated blocks, date and time.

Individual field sampling team members shall be responsible for the care and custody of samples they collect until the samples are properly transferred to the next authorized person or facility. Each time responsibility of a sample changes, the new custodian will sign, date, and note the time that the change occurred on the Chain-of-Custody Record.

Once the complete set of sample aliquots has been collected, they will be placed in an ice-filled cooler for storage and transport to ACZ. Chain-of-Custody record form(s) will be placed in a clear plastic bag (e.g., Ziploc bag), sealed, and placed in the shipping cooler. A signed custody seal will be placed on the outside of each cooler at the opening seam and then securely sealed using shipping tape. One copy of the Chain-of-Custody record will be retained by the Field Team Leader. The original Chain-of-Custody record forms will be returned from the laboratory as part of the final analytical report to Tetra Tech, Inc. This record will be used to document sample custody transfer from the sampler to the laboratory and will become a permanent part of the project file. A copy of the carrier shipping bill shall be retained by the Field Team Leader as part of the permanent Chain-of-Custody documentation.

Upon delivery of the shipping coolers to ACZ, the ACZ Sample Custodian will evaluate the condition of the cooler. The cooler will be opened and the Chain-of-Custody record forms(s) retrieved and signed. The ACZ Sample Custodian then completes a Sample Receipt Form documenting the physical conditions of the shipping cooler and the

sample aliquots, the sample, the pH of the preserved samples, and a radioactivity screen of the samples. Any problems, such as expired holding times, lack of sufficient preservative, improper cooler temperature (i.e., outside the range of  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ), etc. shall be noted on the Sample Receipt Form. The original Sample Receipt Record forms will be returned from the laboratory as part of the final analytical report to Tetra Tech, Inc.

### **5.3 Laboratory Analytical Testing Methods**

Analytes, test methods, preservation techniques, and holding times for surface water samples are summarized on Tables 2a and 2b. The analytes for surface water samples include metals and wet chemistry. Laboratory analyses presented in Tables 2a and 2b are EPA approved, or other widely accepted standard methods. Alternative analytical methods can be proposed and used after review and concurrence with the WQCD. Analytical testing will be performed by ACZ Laboratories, Inc. in Steamboat Springs, Colorado.

## **6.0 CORRECTIVE ACTIONS AND QUALITY**

### **6.1 Failed Chain-of-Custody and Corrective Action**

All issues associated with chain-of-custody procedures are immediately reported to the consultant Project Manager. These include such items as delays in transfer, resulting in holding time violations; violations of sample preservation requirements; incomplete documentation, including signatures; possible tampering of samples; broken or spilled samples, etc. The consultant Project Manager, in consultation with the Project Administrator, will determine when the procedural violation may have compromised the validity of the resulting data. The consultant Project Manager in consultation with the Project Administrator will decide how the issue will be resolved based on best professional judgment. Possible courses of action include, document and proceed; redo the entire sampling event; or selectively analyze samples. The resolution of the situation will be reported to the CBM Consortium at the next regularly scheduled meeting.

### **6.2 Failures in Measurement Systems and Corrective Actions**

Failures in field and laboratory measurement systems involve, but are not limited to such things as, instrument malfunctions, failures in calibration, equipment rinsate blank contamination, quality control samples outside defined limits, etc. In many cases, the field technician or lab analyst will be able to correct the problem. When the problem is resolvable by the field technician or lab analyst, then they will document the problem on the field data sheet or laboratory record and complete the analysis. When the problem is not immediately resolvable, then it is conveyed to the Project Manager, who will make the determination whether the analytical system failure caused invalid results. If the problem is due to laboratory instrument failure, then lab personnel will implement the following corrective actions:

1. The lab will immediately contact the consultant Project Manager to inform him of the nature and potential consequences of the problem.
2. If instrument failure will result in loss of analytical data and there is adequate holding time remaining, the lab will be instructed to send unopened samples to an alternate lab.
3. If alternate sample analyses cannot be performed, the consultant Project Manager will make a decision whether a resample is appropriate and necessary, with concurrence from the Project Administrator. The corrective action plan is intended to ensure that every effort is made to obtain analytical data from all samples. The nature and disposition of problems are reported on the data report that is sent to the consultant Project Manager. The consultant Project Manager will include this information in its next monthly status report to the CBM Consortium.

### **6.3 Quality Control Requirements**

The following sections provide information regarding proper sample collection and laboratory analytical quality control procedures and requirements.

#### *6.3.1 Sample Collection*

Field QC samples are submitted as separate samples to the laboratory and reported accordingly on the data reports per the sample designation procedures described in Section 5.1. Specific requirements of duplicate and equipment rinsate blank samples are discussed below.

Field duplicates - A routine water quality monitoring field duplicate is defined as a second sample, from the same location, collected as part of the same sample aliquot, using identical techniques. This applies to all cases of routine surface water collection procedures. Duplicate sample bottles will be filled in approximate 20 percent increments until each bottle is filled to maximize sample comparability. Duplicate samples are sealed, handled, stored, shipped, and analyzed in the same manner as the primary sample. Precision of duplicate results is calculated by the relative percent difference (RPD) as defined by 100 times the difference (range) of each duplicate set, divided by the average value (mean) of the set. For duplicate results,  $S_1$  and  $S_2$ , the RPD is calculated from the following equation:

#### **Equation 1 Field Relative Percent Difference**

$$RPD (\%) = \frac{|S_1 - S_2|}{(S_1 + S_2) / 2} \times 100$$

Where:  $S_1$  = sample concentration  
 $S_2$  = duplicate concentration

An RPD control limit of 20 percent is used for duplicates comprised of aqueous matrices. For aqueous sample values less than five times the method detection limit (MDL), the RPD method is not applicable and the control limit for the duplicate analysis is set as the sample concentration  $\pm$  the MDL.

Equipment Rinsate Blanks (ERB) – ERBs assess the representativeness of a field sample. An equipment rinsate blank will be generated during each sampling event. A field rinsate blank (environmental blank) may be generated at the discretion of the sampling crew if they believe the potential exists for ambient environmental conditions (e.g., dust) to bias the sample results. Blank samples will be generated with de-ionized water obtained from the laboratory. The laboratory also utilizes blank samples as part of the calibration process (Calibration Verification Blanks) and the method performance process (Method Verification Blanks).

If an analyte is detected in a field blank sample, then sample results within a factor of 10 times the concentration found in an associated blank may be considered undetected, based on a review of additional field and laboratory information.

### 6.3.2 Laboratory Measurement

Detailed laboratory QC requirements are contained within each laboratory Quality Assurance Plan and are also specified in the EPA-approved analytical methods. The minimum requirements that all participants abide by are stated below.

Laboratory duplicate - 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 percent of samples analyzed. Precision is calculated by the relative percent difference (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,  $S_1$  and  $S_2$ , the RPD is calculated from the following equation:

#### Equation 2 Laboratory Relative Percent Difference

$$\text{RPD (\%)} = \frac{|S_1 - S_2|}{(S_1 + S_2) / 2} \times 100$$

Where:  $S_1$  = Laboratory sample concentration  
 $S_2$  = Laboratory duplicate concentration

Laboratory Control Standard (LCS) - A laboratory control sample is analyte free water spiked with the analyte of interest prepared from standardized reference material. The laboratory control standard 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 Percent Recovery (%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 used to calculate percent recovery, where %R is percent recovery includes SR as the sample result and SA as the spike added:

### Equation 3 Laboratory Control Sample Percent Recovery

$$\text{Percent R} = \text{SR} * 100/\text{SA}$$

Where: R = Recovery  
SR = Sample Result  
SA = Spike Added

Matrix spikes (MS) - A matrix spike 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 calculated by Percent Recovery %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 percent recovery, where %R is percent recovery; 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

$$\text{Percent R} = [(\text{SSR} - \text{SR})/\text{SA}] * 100$$

Where: R = Recovery  
SSR = Spiked Sample Concentration  
SR = Sample Result  
SA = Spike Added

Method blank- 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 five percent 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 methods. The requirements for these samples, their acceptance criteria, and corrective action are method-specific and are therefore not listed in this plan.

### 6.3.3 Quality Control Failures and Corrective Action

The Project Manager, in consultation with the Project Administrator, evaluates all sampling QC excursions. In that differences in duplicate sample results are used to assess the entire sampling process, including environmental variability, the arbitrary rejection of results based on pre-determined limits is not practical. Therefore, judgment will be relied upon in evaluating results. Rejecting sample results based on wide variability is a possibility. Notations of field duplicate excursions are noted in the consultant's monthly status report and annual data report. The laboratory staff evaluates laboratory measurement failures. The dispositions of such failures and conveyance to the CBM Consortium are discussed under Failed Analytical Systems and Corrective Action section.

## 6.4 Instrument and Equipment Testing/Maintenance

All sampling equipment testing and maintenance requirements are detailed in Section 6.4. Equipment records are kept on all field equipment and a supply of critical spare parts is maintained. All laboratory tools, gauges, instruments, and equipment testing and maintenance requirements are contained within each laboratory's Quality Assurance Manual. Testing and maintenance records are maintained and are available for inspection by Tetra Tech, Inc.

### 6.4.1 Instrument Calibration and Frequency

Detailed laboratory calibrations are contained within each laboratory's Quality Assurance Manual and are also specified in the EPA-approved analytical methods. Table 4 lists field equipment calibrations.

**Table 4 Field Equipment Calibration Requirements**

Analysis	QC Elements	Frequency
pH	Two Point Calibration (pH 4.01 and 10.00)	Each Day
Specific Conductance	447 uS/cm or 1,500 uS/cm*	Each Day

Note: \* = In general, the Purgatoire River stations require 447 uS/cm calibration while tributary locations require 1,500 uS/cm calibration for specific conductance.

Operation and maintenance of the continuous flow and water quality monitoring equipment includes cleaning the water quality probes and the bubbler-type gages weekly and calibration at least once per month, replacement of chloride probe sensors every five months (Station PR-37.1 only), and rating curve development and calibration for streamflow monitoring.

## **6.5 Supply Inspection and Acceptance Requirements**

The procurement of 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. As applicable, procurement documents include: a definitive scope of work; administrative requirements; technical requirements describing items to be furnished; applicable quality requirements for the supplier(s); right of access to supplier's facilities and records for the purposes of inspections and audit; and documents to be provided by the supplier in support of compliance to procurement requirements. Procurement documents are reviewed by the Project Manager to ensure they include appropriate and adequate provisions to meet intended requirements.

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 clearly identified as such in order to prevent their use. All documentation regarding quality received with the items shall be maintained as quality records and shall be traceable to the items procured via lot numbers, bar codes, or other appropriate system. Examples of these types of records include documentation related to cleanliness levels of equipment and sample containers.

## **6.6 Other Data Acquisitions**

In addition to the data collected under this monitoring program, streamflow data will be obtained from the U.S. Geological Survey (USGS) gaging stations<sup>5</sup> located near Stations PR-2.8 and PR-8.8 (Figure 2). Data obtained from the USGS gaging stations will be utilized during the data evaluation and reporting process. Streamflow data obtained from the USGS will be qualified as provisional in the annual data report to indicate that the agencies have not completed verification of the data.

## **7.0 DATA MANAGEMENT, ASSESSMENT AND OVERSIGHT**

### **7.1 Data Management**

Field data sheets are reviewed and signed by the sampling team leader at the end of each sampling event. Field sheets are then given to the consultant Project Manager for review. Any discrepancies noted during this review are promptly resolved. Field and laboratory data are recorded in an Access database developed by the project consultant and are transferred electronically to the respective CBM consortium administrators in conjunction with the final annual monitoring report. A database is maintained by the consultant which contains information on each site visit including (at a minimum) sampling date, sampling time, consultant personnel, volunteer assistance, weather

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<sup>5</sup> USGS gaging stations at PR-2.8 (USGS Station ID: Purgatoire River below Trinidad Lake, CO 07124410) and at PR8.8 near the Long Canyon bridge (USGS Station ID: Purgatoire River at Madrid, CO 07124200).

conditions, subjective stream and reservoir observations or conditions, problems, instrument calibrations, and quality assurance and quality control samples.

The Microsoft Access database is designed so that the majority of the analytical data received from the laboratory can be loaded into the database from laboratory electronic files. Data is analyzed with Excel spreadsheets.

## **7.2 Assessment and Response Actions**

Review of Purgatoire Watershed field activities is the responsibility of the consultant Field Leader, in conjunction with the consultant Project Manager. Each field team will be accompanied and their performance evaluated by one of these individuals once a year. When possible, field technicians in need of performance improvement will be retrained on-site during the evaluation. When errors in sampling techniques are consistently identified, additional training may be scheduled more frequently. All field and laboratory activities may be reviewed by the state, CBM Consortium and other appropriate personnel as requested.

## **7.3 Consultant Reports and Presentations**

The consultant produces an annual basic data report summarizing results of the calendar year monitoring program. This report contains a summary table of mean, standard deviation, and range data results for each sampling site. A summary table from the database will identify any problems encountered in the monitoring program. The quality assurance and quality control results will be summarized and any problem data flagged.

The consultant will attend meetings with the operators to move the permitting and regulatory process forward to meet the monitoring objectives. Meetings with stakeholders and Water Quality Forum “work groups” (i.e. Basic Standards work group to discuss permitting and low flow issues) are also identified in this task to keep discussions and actions moving in accordance with the permitting and regulatory strategy.

## **7.4 Data Validation and Usability**

All data obtained from field and laboratory measurements will be reviewed and verified for integrity and continuity, reasonableness, and conformance to project requirements, and then validated against the data quality objectives. Only those data that are supported by appropriate quality control data and meet the data quality objectives defined for this project will be considered acceptable.

The procedures for verification and validation of data are described below. The Field Leader will be responsible for ensuring that field data are properly reviewed, verified, and submitted in the required format to the Project Manager. Likewise, the Laboratory Supervisor for each laboratory will be responsible for ensuring that laboratory data are reviewed, verified, and submitted in the required format to the Project Manager for

uploading to the project database. The Project Manager is responsible for verifying that field and laboratory data have been entered correctly into the project database and for validating that all data collected meet the data quality objectives of the project.

All data will be verified to ensure they are representative of the samples analyzed and locations where measurements were made, and that the data and associated quality control data conform to project specifications. The consultant staff and management and subcontract laboratories are responsible for verifying the data each task generates or handles. The field and laboratory staff ensures the verification of raw data, electronically generated data, and data on chain-of-custody forms and hardcopy output from instruments.

Verification of data will be performed using self-assessments and peer review, as appropriate to the project task, followed by technical review by the Project Manager. The data to be verified are evaluated against project specifications and are checked for errors, especially errors in transcription, calculations, and data input. Potential outliers are identified by examination for unreasonable data, or identified using computer-based statistical software. When a question arises or an error or potential outlier is identified, the Project Manager is responsible to resolve the issue. Issues that can be corrected are corrected and documented electronically or by initialing and dating the associated paperwork. When an issue cannot be corrected, the task manager consults with the Project Administrator to establish the appropriate course of action, or the data associated with the issue are rejected.

The Project Manager is responsible for validating that the verified data are usable. One element of the validation process involves evaluating the data again for anomalies. The Project Manager may designate other experienced water quality experts familiar with the project to perform this evaluation. Before data validation can be completed the Project Manager must address any suspected errors or anomalous data.

As soon as possible after each sampling event, calculations and determinations for precision, completeness, and accuracy will be made and corrective action implemented if needed. When data quality indicators do not meet the project's specifications, data may be discarded and re-sampling may occur. The cause of failure will be evaluated. When the cause is found to be equipment failure, calibration/maintenance techniques will be reassessed and improved. When the problem is found to be sampling team error, team members will be retrained. Any limitations on data use will be detailed in both monthly status and annual data reports, and other documentation as needed.

When failure to meet project specifications is found to be unrelated to equipment, methods, or sample error, specifications may be revised for the next sampling season.

## **7.5 Communication and Website**

A "Purgatoire Watershed Monitoring Program" website will convey water quality information along with the near real-time satellite data transmitted to the Sutron website

(<http://www.sutronwin.com/Purgatoire/tw/>). Bi-annual meetings with stakeholders will also support the communication goals of the project. The website will be used to communicate progress, news, and water quality and flow data.

## **8.0 STANDARD OPERATING PROCEDURES**

### **8.1 Purpose**

The standard operating procedures (SOP) describe the collection, preparation, and handling of surface water from streams.

### **8.2 Field-Survey Preparations**

All field instruments and meters are calibrated and a maintenance check is performed to ensure proper function. Calibration of the equipment is conducted in accordance with the manufacturers' specifications (The Program Administrator maintains a PDF file on the Manufacturers' Instructions for Calibration). Spare parts are kept on hand while in the field in the event of an equipment malfunction. A record of all calibrations, standardization including standard lots and expiration dates and maintenance is maintained in a file. Information on dates, operator, time, location, comments and recommended maintenance also are recorded for each use. The logbook is inspected regularly by the Project Manager to ensure recommended maintenance is completed. The Project Manager will sign and date the logbook to indicate approval. Several general procedures are applicable to the collection of all surface water samples and are presented below:

1. Prepare all sampling equipment and containers prior to site visit;
2. Follow the sampling plan in every detail;
3. Document steps in the sampling procedures (The Program Administrator will maintain field forms that can be used for documenting sampling procedures);
4. Evaluate site for safety hazards and any physical conditions that may affect sample condition before commencing sample collection;
5. Observe number and location of sample points, landmarks, references, and routes of access or escape;
6. Record pertinent observations, including a sketch, where appropriate, identifying sample locations;
7. Collect samples and securely closing containers as quickly as feasible; and
8. Make field water quality measurements (i.e., pH, temperature, specific conductance) at the source rather than in the containers, whenever possible.

### **8.3 Sample Containers and Preservation**

Refer to Tables 2a and 2b for sample preservatives and holding times for all analytes. All samples will be placed in a cooler containing ice immediately after sample collection.

### **8.4 In-Stream Water Sampling**

The following surface water sample types will be collected:

- Single point grab samples (from streams and reservoirs).
- Equal-width-increment (EWI) grab samples.

Single point grab surface water samples will be collected in accordance with U.S. EPA ERT Standard Operating Procedure No. 2013 (U.S.EPA, 1994), modified as follows. Single point grab samples may be collected from streams of very small width, or from larger rivers when access to the river poses a safety concern (i.e., during high flow). Rather than using the sample container to collect the sample (as is specified in the “Direct Method” sample collection section of SOP No. 2013, a secondary container shall be used to collect a large volume of surface water, from which the sample aliquots are subsequently generated.

The equal-width-increment (EWI) method will be employed on larger rivers when flow rates and depths are low enough to provide safe access to the water. EWI grab samples are collected with a hand-held depth-integrating sampler, using either the multiple-vertical, or single-vertical method. The multiple-vertical method is preferred, and will be used until the stream depth becomes so small that the depth-integrating sampler cannot be used. By collecting samples at several locations across the width of the stream, and at different depths, the EWI method produces a surface water sample that is discharge-weighted both vertically and laterally. For stream depths too shallow to allow use of the depth-integrating sampler, grab samples are collected from a single depth across the width of the stream. For the EWI, multiple-vertical and single-vertical methods, the sample components are combined in a secondary container (i.e., new one gallon distilled water jug) for processing. Specific procedures for the EWI methodology are provided in the *USGS Open-File Report 90-140 Methods for Collection and Processing of Surface-Water and Bed-Sediment Samples for Physical and Chemical Analyses (USGS, 1990)*.

Sample sites located in standing water or near stream banks will be avoided. Sampling from the upstream side of a bridge aids in the prevention of contamination of the sample from paint chips or dirt from the road. Surface water sampling data, including measurements of pH, specific conductance, temperature, etc. are recorded on the “Surface Water Sampling Record” field form (Appendix A); including documentation of filtration and preservation (sample preservation requirements are summarized in Tables 2a and 2b).

## **8.5 Flow Measurements**

Stream-gaging procedures will be conducted in accordance with ASTM standard D3858-95 (reapproved in 2014) Standard Test Method for *Open-Channel Flow Measurement of Water by Velocity-Area Method* (ASTM, 1995) for flow conditions generally greater than 0.5 cubic feet per second (cfs) or approximately 250 gallons per minute (gpm). Stream gaging procedures utilize a current meter to measure the velocity of the water at a section of the stream that is relatively straight and unobstructed. Velocities will be measured at six-tenths depth for water that is less than 2.5 feet deep, and at two- and eight-tenths depth when the water is greater than 2.5 feet deep. The discharge will then be computed by multiplying the cross sectional area by the velocity of the particular subsection. In general, a minimum of 20 subsections will be measured at each station and, ideally, no subsection will have greater than 10 percent of the total stream flow.

For flows generally less than 0.5 cfs or where the channel may be too shallow for use of a current meter, a portable cutthroat flume will be used to measure stream flows. The flume will be positioned in the stream, leveled, and allowed to equilibrate before readings are collected (Skogerboe, et al., 1973; Baski, Inc., 1997) Flow measurement data will be recorded on the “Surface Water Flow Record” field form (Appendix A).

## **8.6 Field Measurements**

Field measurements of indicator variables consist of specific conductivity (SC), temperature, and pH. Measurements of pH are recorded to the nearest 0.1 of the appropriate units; temperature is recorded to the nearest 0.5° C. Use, calibration, and maintenance procedures follow the manufacturer instructions. Field measurements are taken at the source whenever possible or from the holding container used for sample collection prior transferring the sample to the sample containers. All water quality meters are calibrated and proper function ensured prior to leaving for the field. Upon arriving at the first sample location the instrument is calibrated and the results documented on the field log. Surface water field measurements of pH, specific conductance, temperature, etc. are recorded on the “Surface Water Sampling Record” field form (Appendix A).

## **8.7 Field QA/QC Samples**

The goal of the QA/QC program is to ensure the accuracy, precision, completeness, representativeness, and comparability of sampling data. In order to document the consistency and accuracy of analytical data generated by the laboratory, each team will collect field duplicate and equipment rinsate blank samples for QA/QC purposes during each event.

### **8.7.1 Field Duplicates**

A double volume of water is collected at the appropriate sampling site. The sample is then processed into identical containers by filling approximately 20 percent of each bottle at a

time and then given different location identification names (PR8.8-051510 vs. PR8.8-051510D). Both samples are submitted to the laboratory for identical analyses.

### *8.7.2 Field Blanks*

A volume of laboratory distilled water is taken to the field and placed in an identical sample container using the sampling techniques employed for standard sampling. Samples are sent to the lab identified as “FB” for the sample station followed by the date (i.e., FB-051510). A field blank may be generated at the discretion of the sampling crew if they believe the potential exists for ambient environmental conditions (e.g., dust) to bias the sample results.

### *8.7.3 Equipment Rinsate Blanks*

Equipment rinsate blanks (ERB) are prepared for metals analyses to determine potential sample contamination that may be associated equipment used during sampling. Equipment used for sampling is initially decontaminated (see Section 8.8) and rinsed with laboratory-supplied distilled water. Once decontaminated, the laboratory distilled water is agitated in the sample equipment (e.g., EWI sample containers, distilled water jug). The water that has contacted the sampling equipment is then processed using the sampling techniques employed for standard sampling. Team 1 and Team 2 are required to collect an ERB. Samples are sent to the lab identified as “ERB” for the sample station followed by the team number then followed by the date (i.e., ERB1-051510). Only metals analyses are performed on the ERB samples.

## **8.8 Sampling Equipment Decontamination**

Sampling equipment that comes in contact with environmental media will be thoroughly cleaned before use in the field and between sampling stations. U.S. EPA Standard Operating Procedure No. 2006 (U.S.EPA, 1994), will be followed as modified below.

1. Rinse with tap water or deionized water.
2. Rinse equipment with a dilute (1-5 percent) nitric acid (HNO<sub>3</sub>) solution.
3. Rinse three times with deionized water.
4. Thoroughly rinse with sample water a minimum of three times prior to sampling.

The cleaned sampling equipment will be bagged between sampling stations to avoid environmental contamination. Personnel involved in sampling equipment preparation and sample collection and processing will wear nitrile gloves to protect themselves and to minimize the opportunity for sample contamination.

## **8.9 Gaging Station Operation**

Tetra Tech, Inc. will operate and maintain the seven continuous monitoring stations identified in Table 1.

Gage stations will incorporate a Sutron Accubar constant flow bubbler-type pressure gage that measures the depth of streamflow and converts the depth to an appropriate discharge. Continuous water quality (i.e., pH, temperature, specific conductivity, and chloride) monitoring will utilize a Hach DS-5 Multiprobe. Data measured by flow and water quality equipment will be stored on Sutron 9210 data collection platforms (DCP) at 15-minute intervals.

The gage is housed in a 4x4x8 foot steel shelter. The gaging station is independently powered by two 15-watt solar panels and a 12-volt battery, and is equipped with a radio and antennae for data transmission from the Sutron 9210 unit.

Gages will be cleaned weekly and calibrated and inspected monthly. Tetra Tech, Inc. will maintain the gaging station in a manner consistent with ASTM Standard D5674-95 (reapproved in 2008), Standard Guide for *Operation of a Gaging Station*.

## 9.0 REFERENCES

- ASTM, 1995, “*Standard Guide for Operation of a Gaging Station*,” D5674-95, Reapproved 2008.
- ASTM, 1995, “*Standard Test Method for Open-Channel Flow Measurement of Water by Velocity-Area Method*,” D3858-95, Reapproved 2014.
- Baski Water Instruments, Inc., “*18 Inch Long Cutthroat Flume*,” March 1997.
- Colorado Department of Public Health and Environment, Water Quality Control Commission, “*Regulation No. 31, The Basic Standard and Methodologies for Surface Water*”, 5 CCR 1002-31, effective January 31, 2013.
- Colorado Department of Public Health and Environment, Water Quality Control Commission, “*Regulation No. 32: Classification and Numeric Standards for Arkansas River Basin*,” 5 CCR 1002-32, effective April 30, 2014.
- Colorado Water Quality Control Division, 2008, “*Policy No. WQP-24, Implementing Narrative Standards in Discharge Permits for the Protection of Irrigated Crops*”, March.
- Skogerboe, G.V., Bennett, R.S., and Walker, W.R., 1973, “*Selection and Installation of Cutthroat Flumes for Measuring Irrigation and Drainage Water*,” Colorado State University Experiment Station, December.
- U.S. Geological Survey, 1990, “*Methods for Collection and Processing of Surface-Water and Bed-Material Samples for Physical and Chemical Analyses*,” Open File Report 90 – 140.
- U.S. EPA, 1991, “*Compendium of ERT Surface Water and Sediment Sampling Procedures*,” EPA/540/P-91/005, Office of Emergency and Remedial Response, January.
- U.S. EPA, 1994, “*Sampling Equipment Decontamination*,” EPA ERT SOP #2006, August.
- U.S. EPA, 1994, “*Surface Water Sampling*,” EPA ERT SOP #2013, November.
- U.S. EPA, 2006, “*Guidance on Systematic Planning Using the Data Quality Objectives Process, EPA QA/G-4*,” Office of Environmental Information, EPA/240/B-06/001, February.
- U.S. EPA, 2010, “*U.S.EPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review*,” USEPA-540-R-10-011, Office of Superfund Remediation and Technology Innovation (OSRTI), January.

Wagner, R.J., Boulger, R.W., Jr., Oblinger, C.J., and Smith, B.A., 1997, "Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting," U.S. Geological Survey Techniques and Methods 1-D3.

# APPENDIX A – SAMPLING FORMS

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<b>HYDROLAB CALIBRATION RECORD</b>					<b>STATION No.</b>				
Project No: 133-29603-12002			Location: Purgatoire River Watershed Monitoring			Page of			
Date:		Weather Conditions:			Personnel:				
Comments:									
FIELD INSTRUMENTS USED									
Instrument	Manufacturer/Model		Circle Serial Nos.		Calibration @				
pH Meter	Orion 261		1324931		Std: 4 7 10 @ _____ deg C Reading: _____		% Slope		
pH Meter	YSI 556				Std: 4 7 10 @ _____ deg C Reading: _____				
Specific Conductance Meter	Cole-Parmer CON 400		321739		Std: _____ uS @ 25 deg C Reading: _____				
Specific Conductance Meter	YSI 556				Std: _____ uS @ 25 deg C Reading: _____				
Temperature:	Cole-Parmer CON 400		321739						
Other:	YSI 556								
HYDROLAB CALIBRATION STANDARDS									
pH Buffers (circle)			Conductivity Standard	Chloride Standard (2 point)		Replace pH Reference Standard/Salt Tablets			
4	7	10	_____ 0 and 1,412 _____ uS	_____ 46.2 _____	_____ 319.3 _____	YES	NO		
				mg/L	mg/L	Replace Membrane: YES NO			
HYDROLAB (USING HAND HELD UNIT) & FIELD INSTRUMENT READINGS "BEFORE" CALIBRATION AND CLEANING									
Instrument	Time	pH	Temp. (°C)	Conductivity (uS)	Chloride (mg/L)	Stage (ft)		Meas. Time	
Hydrolab						Staff (ft):			
						Bubbler (ft):			
Field Instrument					---N/A---	---N/A---	---N/A---	---N/A---	
HYDROLAB (USING HAND HELD UNIT) & FIELD INSTRUMENT READINGS "AFTER" CALIBRATION AND CLEANING									
Instrument	Time	pH	Temp. (°C)	Conductivity (uS)	Chloride (mg/L)	Stage (ft)		Meas. Time	
Hydrolab						Staff (ft):			
						Bubbler (ft):			
Field Instrument					---N/A---	---N/A---	---N/A---	---N/A---	
HYDROLAB CONDITION /MAINTENANCE (i.e. probe condition, instrument cleanliness, cleaning methods)									
	pH 7.00	pH 10.00	Conductivity	Chloride			Chloride		
	7.00	10.00	0 & 1,412 uS	46.2 mg/L Activity (50 Actual)*			319.3 mg/L Activity (354.5 Actual)*		
				Conc (mg/L)	Temp (°C)**	mV	Conc (mg/L)	Temp (°C)**	mV
<b>During Calibration:</b>									
<b>Post-Calibration:</b>									
<b>Calibration Status:</b>									
<b>Difference in mV readings (319.3 mg/L - 46.2 mg/L)***:</b>									
Acceptable mV range at Chloride solution temperature (Hach sheet):									
Notes: * = Calibrate to "Activity" concentration, but probe should read "Actual" concentration following calibration.									
** = Chloride solutions must be within +/- 0.2°C for proper calibration.									
*** = Difference in mV readings must meet Acceptance Criteria specifications to properly calibrate chloride sensor (see other side of form).									
<b>Gage Station Checklist Items</b> (circle and comment)									
<b>Control Condition (e.g., clear, debris, ice, channel scour, sediment deposition):</b>									
<b>Hydrolab Condition (e.g., sediment, calcium buildup, algae, probes covered):</b>									
<b>Bubbler Line Condition (free or obstructed):</b>									
Orifice Maintenance: 1) Remove debris_____, 2) Cut end/clear with wire_____, 3) Purge bubbler line_____.									
Desiccant Life Remaining (%): _____									
Wash solar pannels and check for leakage _____									
Instrument Errors: YES NO Comment:									
Comments (e.g., overall gage condition, repairs, general channel conitions, etc.):									
Equipment Decontamination: Simple Green / 1N HCl Wash for _____ Minutes / Other:									
Signature of Field Personnel:					<b>TETRA TECH</b>				
					Longmont, CO (303) 772-5282				

<b>SURFACE WATER SAMPLING RECORD</b>						<b>SAMPLE No.</b>			
Project No: 133-29603-12002 Task 1			Location: Purgatoire River Watershed Monitoring			Page of			
Date:		Weather Conditions:			Personnel:				
Comments:									
INSTRUMENTS USED									
Instrument	Manufacturer/Model	Circle Serial Nos.	Calibration @						
pH Meter	Orion 261	1324931	Std: 4 7 10 @ _____ deg C reading: _____ Slope:						
pH Meter	YSI 556		Std: 4 7 10 @ _____ deg C reading: _____						
Specific Conductance Meter	Cole-Parmer CON 400	321739	Std: _____ uS @ 25 deg C reading: _____						
Specific Conductance Meter	YSI 556		Std: _____ uS @ 25 deg C reading: _____						
Temperature	Cole-Parmer CON 400	321739							
Other:									
DATA FROM RECORDING GAGE									
Date	Time	Stage	Discharge from table	Shift	Discharge with shift	Specific Conductance	pH	Temperature	Chloride
SAMPLING INFORMATION									
Sampling Equipment: Geopump, Jumpit, Cflex tubing, New 1 gallon DI jug									
Filtration: Geotech 0.45 micron in-line high capacity disposable filter. Masterflex Cflex tubing.									
Comments: Store DI jug rinsed 3 times with sample water prior to sampling.									
SAMPLING MEASUREMENTS:									
Date/ Time	Type of Sample <small>(Grab/Composite)</small>	Depth Sampled <small>(feet below surface)</small>	pH	Specific Conductance		Temp <small>(deg C)</small>	Other	Comments <small>(color, sediment, etc.)</small>	
				<small>(uS @ Field Temp.)</small>	<small>(uS @ 25 deg C)</small>				
				-----					
SAMPLE HANDLING:									
Date/ Time	Aliquots			Filtered <small>(Yes/No)</small>	Preserved <small>(type)</small>	Comments			
	Volume	Bottle Composition	Quantity						
	500 mL	HDPE	1	No	None	No Color Code, Wet Chemistry			
	250 mL	HDPE	1	Yes	None	White Dot, Wet Chemistry (Dissolved)			
	250 mL	HDPE	1	No	HNO <sub>3</sub>	Red Dot, Metals (Total recoverable/Total)			
	125 mL	HDPE	1	Yes	HNO <sub>3</sub>	Green Dot, Metals (Dissolved)			
Field QA/QC Samples Collected (Sample No., Type, Date/Time, Method):									
SAMPLING LOCATION									
Number of photographs taken:			North:  Scale:						
Description:									
Equipment Decontamination:									
Signature of Field Personnel:					<b>TETRA TECH</b> Longmont, CO (303) 772-5282				

