
**West Fork of the Gallatin River Nutrient Assessment
Sample and Analysis Plan (SAP)**

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Sampling and Analysis Plan West Fork of the Gallatin Watershed Nutrient Assessment

This document constitutes the Sampling and Analysis Plan (SAP) for an in-stream nitrate processing/uptake investigation in the Upper Gallatin TMDL Planning Area. This investigation will provide information necessary to parameterize a Nutrient Export Model in the Upper Gallatin watershed.

1.0 Introduction and Background

The West Fork Gallatin River, a tributary to the Gallatin River, is situated in the northern Rocky Mountains of southwestern Montana. The West Fork Gallatin (212 km²) watershed consists of three main tributaries: the South Fork Gallatin (121 km²), the Middle Fork Gallatin (48 km²), and the North Fork Gallatin (24 km²). The West Fork Gallatin River watershed is home to several resort communities and is experiencing rapid growth and development within its boundaries.

Nutrients, such as nitrogen and phosphorus are essential to stream biota activity. However, when a stream has an excess of nutrients the stream loses the ability to utilize the excess nutrient and it is flushed downstream, increasing nutrient loads to downstream water bodies (Earl, et al., 2006).

In-stream nitrogen (N) processing varies with stream characteristics. As stream size increases so does velocity, which can decrease nutrient uptake (Ensign and Doyle, 2006). Also, stream uptake depends on ambient nitrogen levels; stream uptake rates decrease as the stream approaches nitrogen saturation (Earl et al., 2006). Other studies have demonstrated that nutrient uptake can vary substantially between seasons within the same stream reach (Simon, et al., 2005, Mulholland et al. 1985). In areas of rapid development, such as in the West Fork watershed, anthropogenic nutrient additions can be large. Even modest additions can increase concentrations downstream, especially between seasons (Kaushal et al., 2006).

One component to understanding and predicting the fate and transport of nutrients in such environments is investigating and quantifying how nutrients are assimilated or cycled through in-stream processes. To determine the cycling of nutrients in stream ecosystems where hydrologic and nonhydrologic processes determine nutrient fate (Runkel, 2007), nutrient addition experiments are used. **This *Sampling and Analysis Plan* documents methods and procedures whereby a nitrate (KNO₃) addition will be conducted in the selected streams of the West Fork in order to quantify NO₃⁻-N uptake lengths for each selected reach.** The data from the nutrient addition experiments will be used to further calibrate and parameterize a nutrient export model that will be used to estimate nutrient loading from a variety of land use categories in the watershed (DEQ contract 205049).

1.1 Nutrient Export Model Description

Nutrient sources associated with specific land uses in the Upper Gallatin Watershed will be identified through a nutrient export model. The land use/land cover and watershed characteristics (watershed residence times and riparian area) of the contributing area to each

sampling point discussed above will be determined and implemented into a nitrogen export coefficient model to determine their relationships with the water quality data. The nitrogen export coefficient model is adapted from a mechanistic and spatial modeling approaches used by Worrall and Burt (2001) and Endreny and Wood (2003). In the model, the N export (NE) to sample point m (lower end of stream reach) is a function of (eqn. 1):

$$NE_m = \left(\sum_{i=1}^n LULC_i * E_i + (S_i * s) + (W_i * w) * TWF * RBI \right) + \left((NE_{m-1}) \exp^{\frac{K_L X}{Q^{0.5}}} \right) \quad (1)$$

where **LULC** is the land use/land cover in grid cell i , **E** is the export coefficient of **LULC**, **S** _{i} is the number of septic systems in the pixel, **s** is the septic NO₃⁻ load, **W** _{i} is a wastewater coefficient (1 if wastewater is distributed on the cell, 0 if not), **w** is the wastewater NO₃⁻ load, **TWF** is a topographical weighting factor of grid cell i , and is a scaled combination of the TT index (**TT**), and the topographic index (**TI**), **RBI** is a riparian buffer index ratio *only activated if land upslope contributing area is not pristine*, and **N** _{$m-1$} is NO₃⁻ load from the upstream sampling point. **NE** _{$m-1$} will decay exponentially as a function of stream uptake rate (**K** _{L}), distance (**X**), and is a function of stream size (specifically stream discharge **Q**^{0.5}) (Wollheim et al., 2001). In the first model approximation, **K** _{L} and **Q**^{0.5} will be based on literature values to be tested and updated with field results from instream tracer additions determined in this investigation.

This model calculates **NE** (N export) (eqn. 1) to location **m** (the end of each stream reach) by incorporating two major elements: Lateral loading of N to each stream reach (eqn. 2) and upstream loading (eqn. 3) of N to each stream reach (**m-1**).

$$\left(\sum_{i=1}^n LULC_i * E_i + (S_i * s) + (W_i * w) * TWF * RBI \right) \quad (2)$$

$$\left((NE_{m-1}) \exp^{\frac{K_L X}{Q^{0.5}}} \right) \quad (3)$$

In the initial model approximation, only the load entering the reach from upstream is subject to uptake in each reach (**NE** _{$m-1$}). Lateral inflows are subject to instream uptake in the next downstream reach. The model will be run for each stream reach and synoptic sampling point. The total watershed export for the West Fork watershed is then the **NE** _{m} for the last stream reach in the watershed and represents the integrated watershed response.

The validated model will: 1) identify relationships between distribution of LULC, watershed characteristics, water quality, 2) identify nutrient sources to assist in TMDL nutrient load allocations, and 3) quantify map nutrient export risk according to spatial location and distribution of LULC and watershed characteristics.

2.0 Overview of Sampling Strategy

The objective of this sampling plan is to provide nutrient uptake data to develop empirically-based coefficients to support the nutrient export model (Section 1.1). Stream sampling and analysis will be conducted with the objective of determining in-stream nutrient processing, specifically NO_3^- -N, in order to calibrate and parameterize the nitrogen export model. The procedures for a nutrient addition experiment are described in detail in Webster and Valett (2006) and briefly summarized in Payn et al. (2005).

2.1 *Sampling locations*

Nutrient uptake will be determined by nutrient enrichment tracer injections, and will take place on four (4) distinct reaches in the West Fork Gallatin watershed. Sampling sites were chosen to represent the range of baseline flow and ambient nutrient levels. Sites were chosen through assessment of available nutrient concentration data already collected in the Upper Gallatin watershed. At two of the sites, a seasonal comparison will also be done, thus six (6) nutrient addition experiments will occur in total. Table 1 shows the four stream reaches, their corresponding characteristics, and the season in which experiments will occur.

Table 1: Location, reach characteristics and season of nutrient enrichment experiments to be conducted in the West Fork watershed.

Streams	Baseline Flow (CFS)	Ambient nitrate levels (ppm)	Season of experiments ¹
Beehive upstream of trailhead	Low (< 5)	Low (< 1)	Summer and Winter
Middle Fork headwaters at Pony Lodge	Low (< 5)	High (≥ 1)	Summer and Winter
South Fork above Yellow Mule inflow	High (≥ 5)	Low (< 1)	Summer only
Middle Fork between the dam below the golf course and bridge on Big Sky Spur Road	High (≥ 5)	High (≥ 1)	Summer only

¹Summer experiments will be conducted between May 15 and August 31; winter experiments will be conducted between October 1 and March 31.

2.2 *Sampling Activity*

Each experiment will be conducted over a 500 to 1000 meter stretch. Experimental reach length will vary between experimental stretches. Reach length is determined by stream size (order and discharge) and ambient nitrate levels; longer stream stretches are needed for higher flow and higher ambient nitrate levels. At each site the following procedures will be conducted (the

procedures are described in detail in Webster and Valett (2006) and briefly summarized in Payn et al. (2005):

- A solution of stream water, a conservative solute (NaCl) and fertilizer (KNO₃) will be mixed in a large carboy until all solids are dissolved. The solution will be added to the stream at a constant rate using an electric pump; the drip is placed in a stretch where the stream is mixing well (i.e. where there is a constriction then a drop then a pool).
- Water samples are grabbed before the addition begins at the nutrient addition site (0 meters) and at the end of the experimental reach for determining ambient NO₃-N concentration levels.
- Electrical conductivity (EC) is measured continuously at three sites (10-20 meters above 0m, 20-30 m below 0m and at the endpoint (500 m to 1000 m downstream from 0m)) during the experiment.
- Once EC reaches a steady-state, one sample will be taken at ten (10) evenly spaced sites between 0 m and the end point. Two sites will be randomly chosen, one at which to take a duplicate sample and one to take a blank. A total of twelve samples will be collected during steady-state.
- The data collected from the EC probes and the water samples will be used to calculate an estimate for NO₃⁻-N uptake length (S_w) for each stream stretch.
- Samples collected during the experiment will be surveyed for NO₃-N and Cl⁻ in the water column.

An alternate method may have to be used in the streams with high flow. This method includes these procedures:

- A solution of stream water, a conservative solute (NaCl) and fertilizer (KNO₃) will be mixed in a large carboy until all solids are dissolved. The solution will be added to the stream at one time as a slug; the slug is poured in a stretch where the stream is mixing well (i.e. where there is a constriction then a drop then a pool).
- Water samples are grabbed before the addition begins at the nutrient addition site (0 meters) and at the end of the experimental reach for determining ambient NO₃-N concentration levels.
- Electrical conductivity (EC) is measured continuously at three sites (10-20 meters above 0m, 20-30 m below 0m and at the endpoint (500 m to 1000 m downstream from 0m)) during the experiment.
- After the slug is injected, water samples are collected every 2-10 minutes depending on the slope on the curve of the real-time EC data being collected by the data logger and displayed on a laptop. The samples are collected at the endpoint (500 m to 1000 m downstream of the slug injection).
- With at least two randomly chosen samples, a replicate will be grabbed at the same time. If number of samples exceeds 20, then more replicates will be taken so that 10% of samples collected have replicates. A blank sample will also be obtained.
- The data collected from the EC probes and the water samples will be used to calculate an estimate for NO₃⁻-N uptake length (S_w) for each stream stretch.
- Samples collected during the experiment will be surveyed for NO₃-N and Cl⁻ in the water column.

2.3 *Chemical data*

Stream samples will be analyzed for nitrate-N (NO_3^- -N) and chloride (Cl^-). In addition, electrical conductivity (EC), temperature and flow will be collected at the time of the nutrient addition experiment.

3.0 Field Sampling Methods

Each person involved in field sampling will be trained in the sample collection methods by the PI. These methods include:

- Marking each bottle with sample site, date and time
- Sampling above any disturbance including his/herself
- Sampling in flowing water in main channel
- Rinsing bottle and cap three times with stream water before drawing a sample
- Keeping hands out of bottle and cap
- Recording date, time, weather and any other observations in the field notebook
- Placing sample in cooler immediately after collection

We will take duplicates at two of the sampling sites during the steady-state sample collection; this will surpass the 10% field duplicates requirement.

Stream discharge data will be calculated at the top and bottom of the experiment stretch before the nutrient addition begins by adding a known mass of NaCl (chloride is a conservative tracer and should not be lost to uptake) and integrating area under the curve read by an EC probe.

Conductivity and temperature will be measured with Campbell Scientific CS547A Conductivity and Temperature Probes at three sites: 10-20 m above the injection point, 20-30 m below the injection point and at 500 m (the end of the experimental stretch). The EC probe is calibrated using a regression relationship between EC of NaCl measured in the lab and in the field.

4.0 Sample Handling Procedures

Samples will be immediately put on ice by the sample collector, and all of the samples at the end of a sampling event will be collected by a project PI who will transfer to the laboratory. If the samples are not filtered on site, once at the laboratory, each sample is filtered with a 4 micron filter into a sterile bottle and immediately frozen until analysis. All lab assistants involved in the filtering of samples will be trained by a project PI in the appropriate methods of filtering samples including: wearing gloves, changing the filter after each sample, filtering into sterile bottles, and note-taking of any potential mishaps that may occur.

5.0 Laboratory Analytical Methods

Montana State University Geomicrobiology and Geochemistry Laboratory (Bozeman, MT)

Chloride (Cl^-) and nitrate-N (NO_3^- -N) will be analyzed at the Montana State University Geomicrobiology and Geochemistry laboratory. They will be analyzed by ion chromatography (U.S. EPA, 1993) with a Metrohm-Peak compact ion chromatograph (IC).

A summary of analytical methods is provided below in **Table 1**.

Table 2: Summary of analytical methods for NO₃⁻ and Cl⁻

Nutrient Samples: Sample Volumes, Containers, Preservation and Analytical Methods				
Analyte	Sample Volume	Container	Preservation	Analytical Method
NO ₃ ⁻	60 ml	Acid-washed polyethylene	Cool to <10C, filter. Freeze.	EPA 300.0
Anions (Cl ⁻)	60 ml	Acid-washed polyethylene	Cool to <10C, filter. Freeze.	EPA 300.0

6.0 Quality Assurance and Quality Control Requirements

Data quality objectives (DQOs) are the quantitative and qualitative criteria established for data in order to meet the project's objectives. There are several categories of DQO including precision, accuracy, representativeness, completeness, comparability, and measurement range. This section describes the approach to ensure data collected for this effort meet a high standard for data quality.

6.1 Precision

Precision refers to the degree of agreement among repeated measurements of the same characteristic. The strategy to ensure a high level of precision involves several components. These include selection of relatively precise measures based on published or unpublished reports. Selection of field meters with demonstrably high precision as reported in the manufacturer's specifications for ranges likely to be encountered in the field is another approach to promote precision. With other parameters, training and adherence to SOPs provides a means to encourage a high degree of precision.

We will follow DEQ SOPs which require collection of duplicates and blanks for 10% of samples collected in the field. The duplicates will be evaluated based on their coefficient of variation. All samples with a coefficient of variation less than 10% will be accepted. Synoptic sampling will occur during steady-state of electrical conductivity. During this synoptic sampling, two samples will be taken at two randomly chosen sites (which will be more than 10% of total samples collected) and one site will be randomly chosen for which to take a blank. Similarly, laboratory methods will follow established QA/QC protocols that evaluate precision in accordance with commonly accepted analytical protocols. These include employing blanks and known NIST standards at the beginning and end of each time period and after every 10 samples analyzed. Statistics will be calculated after a run to assure that the ion chromatograph is measuring consistently throughout a sample run.

6.2 Accuracy and Bias

Accuracy is a measure of confidence that describes how close a measurement is to its "true value". While the true value may not be known, several steps will increase the accuracy of field measures and laboratory analyses. Strict adherence to SOPs, training, oversight by the PI, and

implementation of QA/QC protocols are the primary means of promoting accuracy for physical and chemical assessments.

More water is collected than required for analysis and left over water will be refrozen after analysis. If faulty data is suspected, the left over water will be rerun with the IC and compared to previous data to determine if the suspected error was caused by inaccurate analysis by the IC.

Bias is a systematic error introduced by selecting items from a wrong population or favoring some of the elements of a population. Random sampling described in Section 6.3 and sampling in flowing water will address methods to avoid this type of bias.

6.3 Representativeness

Representativeness refers to the extent to which measurements actually represent the true environmental condition. For example, sampling site selection should reflect the relative proportion of geology, watershed characteristics, and land use. Approaches to promote representativeness include a combination of random sampling, best professional judgment, and adherence to sampling methods described in section 3.0 and 4.0.

6.4 Completeness

Completeness is a measure of the amount of data prescribed for assessment activities and the usable data actually collected, expressed as a percentage. QA/QC activities will promote a high degree of completeness for assessments in the Upper Gallatin drainage. A PI will be responsible for ensuring collection of all data for each site. Prior to leaving a sampling site each field person will be required to fill out a data sheet, which will be reviewed and initialed by the project manager. These checks will reduce the occurrence of empty data fields.

6.5 Measurement Range

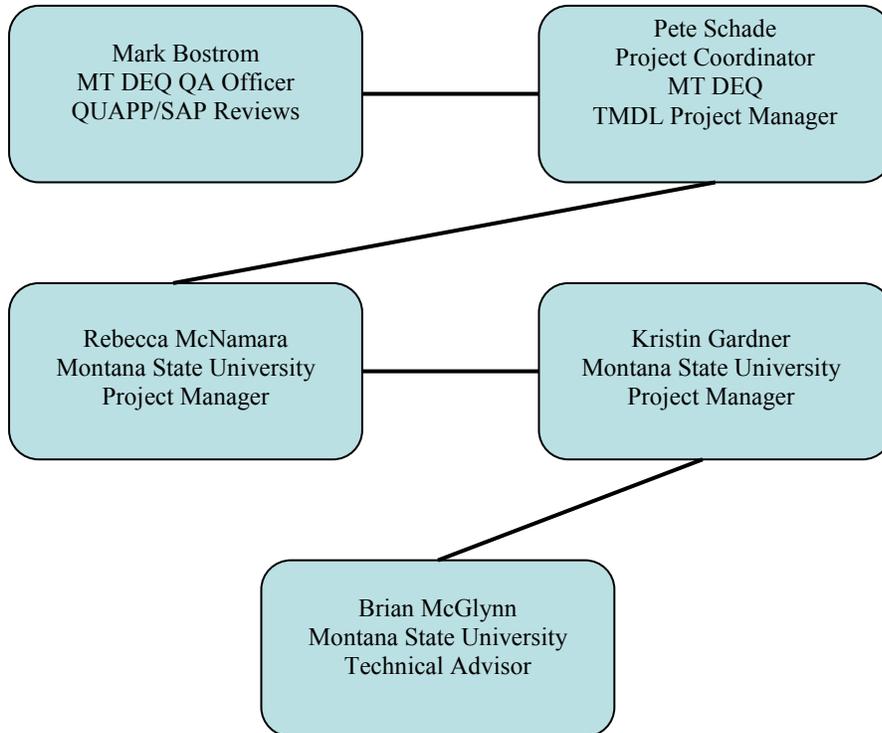
Detection limits for both of the anions will be determined by the Method of Detection Limit described in the ARM referenced method at 40CFR Part 136, Appendix B Rev 1.11.

7.0 Data Analysis, Record Keeping and Reporting Requirements and Schedule for Completion

All field notes are kept by the PI. All flow, EC, and temperature data is in the PI's field notebook and input into a spreadsheet. All flow, EC, temperature, and results of the ion chromatograph are kept in excel spreadsheets and an access database that is backed up on a weekly basis.

All field work will be completed by the December of 2008. Data analysis will be completed by the end of the year 2009. Data from all sampling events will be provided to be uploaded to STORET via Montana Web-SIM. Details for data upload to STORET can be found on DEQ's website at http://www.deq.state.mt.us/wqinfo/datamgmt/STORET_SIM_Support.asp.

8.0 Project Team and Responsibilities



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