Monitoring and Reporting Plan
Central Coast Irrigation and Nutrient Management Program, Santa Maria Watershed

SWRCB Agreement Number 14-475-553
City of Santa Maria
April 2016

Introduction

This Monitoring and Reporting Plan was prepared for the State Water Board Grant Agreement number 14 – 475 – 553 granted to the City of Santa Maria for the purpose of treating agricultural drainage water to reduce pollutant loading to surface and groundwater within the City of Santa Maria. This document identifies the nonpoint sources of pollution to be prevented or reduced by the project, describes the baseline water quality to be addressed, describes how this project will be effective in preventing or reducing pollution and in demonstrating the desired results, and describes the monitoring program including methodology, frequency, and duration of monitoring.

The Monitoring and Reporting Plan is accompanied by a Project Assessment and Evaluation Plan (PAEP), which describes the manner in which the project will be effective in preventing or reducing pollution. The Monitoring Plan describes the baseline water quality to be addressed, identifies the nonpoint sources of pollution, and provides GPS information. A Quality Assurance Project Plan has been prepared, and will be maintained, and implemented in accordance with the State Board's Surface Water Ambient Monitoring Program (SWAMP), data reporting requirements, and the United States (US) Environmental Protection Agency (EPA) Quality Assurance Project Plan (QAPP) requirements. Finally, all appropriate data shall be uploaded to the California Environmental Data Exchange Network (CEDEN), and proof of all successful data submission will be sent to the grant manager prior to submitting final invoices.

Monitoring Plan

Central Coast Irrigation and Nutrient Management Program, Santa Maria Watershed
SWRCB Agreement Number 14-475-553
City of Santa Maria

Introduction

The purpose of the project is to implement an agricultural tailwater denitrification system for the treatment of nutrient rich agricultural flows within Jim May Park; and provide pollution prevention and reduction strategies for irrigation and nutrient management in the Santa Maria Watershed. The project involves an integrated regional water management approach to addressing nitrate in agricultural runoff and supporting municipal water supply in a disadvantaged community. The project includes the installation of a denitrification woodchip biofilter that will treat approximately 200 gpm of discharge from 5300 acres of irrigated agriculture and 500 acres of additional land that drain into this channel. Prior to the installation this project, water from Bradley Channel discharged into a large water body constructed for flood control in a city park, named Jim May Park. Water from the water body overflowed into another channel and series of flood control basins prior to discharging into Santa Maria River. Once this project is constructed, water will be intercepted from Bradley channel via a sump and pumped into the head of the woodchip biofilter. As the water travels through the biofilter, a biological process will convert the ammonia and nitrate into nitrogen gas. Once the water leaves the biofilter, it will return the treated tailwater back into Bradley Channel.

The purpose of this monitoring plan is to identify how the City of Santa Maria is going to sample water quality upstream and downstream of a biofilter at Jim May Park to determine the effectiveness of the biofilter at removing ammonia and nitrate from the water.

Background

The Bradley Channel at BCJ (Bradley Channel at Jones) and BCU (Bradley Channel at Magellan Drive) have been actively monitored for several constituents including channel flow, nitrogen species, and other constituents, as part of the Central Coast Ambient Monitoring Program (CCAMP). This data can be found at www.ccamp.org. Bradley Channel at Magellan, the closest CCAMP sampling location to the proposed biofilter, shows a minimum nitrate of 0.32 mg/L a maximum nitrate of 68 mg/L and an average nitrate of 20 mg/L. Samples were collected from 2000 through 2013. Data in more recent years shows higher nitrate than data from previous years. For comparative purposes, the maximum contaminant limit for nitrate in drinking water is 10 mg/L. This data demonstrates the significant nitrogen loading contributed from agricultural land adjacent to Bradley Channel.

There are multiple studies that exist that show varying success of woodchip biofilters to remove nitrate from water. The best success depends on providing the appropriate conditions necessary for full nitrification and then full denitrification. Full nitrification can only happen if there is sufficient carbon, oxygen, and detention time necessary to convert all of the remaining ammonia to nitrate. Full denitrification can only happen if there is sufficient carbon, lack of oxygen, and detention time to convert all of the nitrate to nitrogen gas. In addition, the filter must be sufficiently wet at all times in order to maintain the bacteriological population.

This agricultural tailwater drainage project was designed based off of work previously performed at sites such as the rest stop off Highway 46 in California and El Centro, California. These are smaller scale projects to show that passive woodchip biofilters can successfully remove nitrate from water if designed properly.

The estimated existing mean annual load in Bradley Channel at BCJ is 162,181 lbs and a loading capacity of 82,746 lbs. Dry season loads are estimated at 51,079 lbs with a loading capacity of 15,357 lbs. This project is anticipated to remove approximately 9,000 lbs-N per year.

Overview

City staff have prepared this Monitoring Plan for use by City personnel and water board staff. City personnel are responsible for coordinating and performing the sampling events, including providing sampling equipment, obtaining sample bottles from the lab, taking field notes, and ensuring delivery of the samples to the analytical laboratories. The following sections provide details of the Monitoring Plan, including constituents, sampling locations, frequency, and sampling team. The QAPP will discuss the details of how the samples are collected to provide data that are representative and scientifically defensible.

Water Quality Sampling

Samples will be collected upstream and downstream of the biofilter to characterize water quality associated with irrigation tailwater and the effectiveness of the project. As the project progresses, there may be a need to add or remove sampling sites and to adjust the timing of the sampling events. This Monitoring Plan will be updated with changes to the locations and schedule as needed.

Constituents

A limited list of constituents will be monitored. The list of sampling constituents and rationale for each are summarized in Table 1 below.

Table 1 Sampling Constituents

Constituent	Purpose	Comment
Ammonia	Impacts on Downstream Algae Growth and Dissolved Oxygen; toxicity	Laboratory
Nitrate	Impacts on Groundwater and Downstream Algae Growth and Dissolved Oxygen	Laboratory
Total Nitrogen	Impacts on Downstream Algae Growth and Dissolved Oxygen	Laboratory

Sampling Locations

Sampling sites have been selected at the inlet and outlet of the biofilter to characterize the effectiveness of the biofilter. The sample locations will be documented with GPS coordinates. Table 2 describes the sampling locations.

Table 2 Sampling Locations

Sample Site Designation	Sample Site Location	Purpose and Other Comments
Upstream/Inlet of Biofilter	120°25'28.00" West 34°58' 28.60" North	To characterize the water before treatment
Downstream/outlet of Biofilter	120°25'27.00" West 34°58'30.90" North	To characterize the water after treatment

Based on field conditions, the program may be modified by the project team during the sampling event to provide for field safety and make the collection accurate and thorough. Any changes made to the plan will be documented within the field notebooks and added to this Monitoring Plan as Appendices.

Sampling Frequency and Schedule

Sampling events will be conducted on a two-week basis following construction of the biofilter. Each sampling event requires approximately half a day to collect and record water samples, measure field parameters, prepare samples for transport, and deliver and mail samples for delivery to the respective laboratories. Specific dates on which the sampling events will occur within each month will be determined by City personnel.

Sampling team

The sampling team is composed of one City of Santa Maria Water Systems Operator that collects samples, and measures field parameters. The Water Resources Manager from the City of Santa Maria provides project oversight, is the leader of the sampling team, and provides technical assistance as needed.

Reporting

Results obtained from both the field investigation parameters and laboratory data are to be validated for quality, accuracy, and completeness according to the guidelines set forth in the QAPP document. The data are then to be tabulated in database format compliant with the SWAMP program, saved, and maintained by City or designate personnel. Results of these reports will be provided as described in the grant agreement with the State (SWRCB agreement 14-475-553).

Quality Assurance and Project Plan
City of Santa Maria
Central Coast Irrigation and Nutrient Management Program,
Santa Maria Watershed
Revision 2
~~**December 2015**~~
April 2016

Project Manager	5/3/16 Date
City Quality Assurance Officer	4/29/2016 Date
Grant Manager	5/9/2016 Date
Water Board Quality Assurance Officer	5/9/2016 Date

Distribution List

Name	Title	Organization
Shannon Sweeney	Water Resources Manager	City of Santa Maria
Lisa Long	Business Services Manager	City of Santa Maria
Alexandra Griffith	Regulatory Compliance Supervisor	City of Santa Maria
To Be Determined	Water System Operator	City of Santa Maria
Katie McNeill	Grant Manager	Regional Water Quality Control Board

Project Organization

Individuals involved with this project include:

- Shannon Sweeney, project manager
- Lisa Long
- Michelle Ruiz
- Shad Springer
- City of Santa Maria public works staff
- Design engineer, To be determined (tbd)
- Contractor, tbd
- Sample collectors, tbd
- City of Santa Maria regulatory compliance supervisor (advisory)
- Certified laboratory

Shannon Sweeney is responsible for managing the project, keeping it on schedule, and ensuring that the finished product meets the goals of the grant. She is also responsible for maintaining the official, approved Quality Assurance Project Plan. Lisa Long is responsible for project administration, including paperwork, invoices, and report submittal. Michelle Ruiz provides administrative support, including document review, formatting, and other clerical assistance. Shad Springer supervises all of the aforementioned staff, and provides review and overall direction on the project. The regulatory compliance supervisor, Alexandra Griffith, is the quality assurance officer and is independent of any data generation. Shannon Sweeney, Lisa Long, and Shad Springer are the project team.

Problem Definition

The City of Santa Maria sits on top of a very large groundwater basin called the Santa Maria Valley basin. This area is very heavily used for agriculture, including berries and truck crops. In 2012, several stakeholders within the Valley worked together to produce an assessment of the fate and transport of nitrogen within the Valley (yyhttp://cosb.countyofsb.org/uploadedFiles/pwd/Water/IRWMP/2013_Plan/SM_GW_As

sessment_SN_Report%2010_10_2013%20Final.pdf). That evaluation showed that although the stakeholders are implementing practices to better control the amount of nitrogen entering the surface and groundwater than we were several decades ago, that more nitrogen is currently entering the basin than leaving it, which is resulting in a nitrate buildup within the basin. Such practices include
"1) reducing deep percolation past the root zone, 2) utilizing a higher percentage of the nitrates applied in the root zone, 3) introduction of higher quality water sources, and 4) increased removal of salt and nutrient through water treatment or use techniques." (GEI Consultants, Inc, 2013).

The Santa Maria Valley groundwater basin has several beneficial uses, including agricultural irrigation, and municipal water supply. A continuation of the nitrate buildup within the Valley will negatively affect the city's ability to deliver this water as a domestic supply. It is important that there be mechanisms to pump nitrate out of the ground and convert it to less harmful forms of nitrogen.

Excess algal growth from the nitrate is believed to be responsible for large variations in the pH and dissolved oxygen within the water body at Jim May Park. By reducing the nitrate entering this water body, it is expected that there may also be a decrease in the pH and dissolved oxygen variations, which will make this water body and the downstream Santa Maria River more ecologically viable for native plants and wildlife. The goal of the biofilter is to achieve a nitrate concentration less than 10 mg/L-N, which is the drinking water maximum contaminant level. However, we have reason to believe that the biofilter will achieve better results, based on the results from other such biofilters in the area. If so, then it is possible that the nitrate concentration leaving the biofilter could possibly achieve the dry season nitrate total maximum daily load (TMDL) of 4.3 mg/L-N for the lower Santa Maria River from Highway 1 to Santa Maria River Estuary. As analytical data is received, adjustments will be made to the operation of the biofilter, in an attempt to achieve the lowest nitrate result possible.

Project Description

Sampling of the water quality and flow before and after treatment by the biofilter will be used in order to determine the ability of the biofilter to reduce the nitrogen load in lbs/day. Water from the groundwater well will also be sampled for flow and nitrogen when it is running as it is supplementing the flow to the biofilter. Flow entering from the channel will be determined by subtracting out the well water flow from the total flow entering the biofilter. Sampling cannot begin until the biofilter is complete. Once the biofilter has running water, samples will be collected every other week for one year to verify that the biofilter works through all seasonal conditions. The biofilter is expected to be complete by summer 2016. Samples will be collected once every other week by city staff. We are not anticipating any resource or time constraints. A map of the area is included as Appendix 1.

Quality Objectives and Criteria

Samples will be analyzed by a certified commercial lab, who will analyze the samples per standard methods. Samples will be considered acceptable if they meet the quality assurance and quality control established by the commercial lab and per the criteria included in the following link:

http://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/3_nut_water.pdf

All sample results will be accompanied by a QA/QC from the laboratory. Samples that do not meet the QA/QC will be resampled and reanalyzed. The commercial laboratory's special project method summary and individual analyte methods are attached.

Special Training/Certifications

Samples will be collected by City of Santa Maria staff who are certified treatment or distribution system operators through the State of California. These staff collect samples on a regular basis and will follow standard operating procedures that have been developed for this project. The City maintains proof of certification that they are water system operators. Information is also available on the State's drinking water website.

Documentation and Records

City staff will maintain a spreadsheet and associated graphs showing effectiveness of the biofilter at reducing nitrogen species. These graphs will be printed after each update so that a hard copy is available. All data associated with this project will be kept in its own file folder at the City landfill, located at 2065 East Main Street., Santa Maria. Data will be kept per the record retention requirement of thirty-five (35) years after final payment. The hard copies will serve as a backup for the electronically stored records. The Water Resources Manager will give a current copy of the approved quality assurance project plan to each staff person associated with the project after each update.

Data Generation and Acquisition

The sampling scheme for this project has been designed for two week sampling specifically because that is the length of time it typically takes to populate the biofilter. Samples taken more frequently are not likely to represent the effectiveness of the biofilter, and samples taken less frequently will likely miss seasonal variations in biofilter operation. Samples upstream of the biofilter will be taken at the biofilter inlet. Samples from downstream of the biofilter are best taken at the biofilter discharge (outfall) point.

As can be seen in the CCAMP data there is a considerable amount of variation in the nitrate data. One sample should not be considered representative of the effectiveness

of the biofilter. Rather, it will be important to look at trends, to see how the biofilter operates over time.

Sampling Methods

All sampling for this project will conform to AWWA standard methods, with no modifications. All samples will be grab samples of water. For all analytes, the sample shall be collected in the bottle specified by the method. Samples shall be collected in clean, unused bottles.

All samples shall be placed on ice and shipped to the commercial laboratory the day of collection. If any problems occur in the collection, transit, or contamination of the samples, the sample collector shall discard the sample and resample prior to shipping the sample to the commercial laboratory.

Sample Handling and Custody

Unpreserved samples are placed on ice to achieve a temperature of less than 6°C and transported to the commercial laboratory. Commercial laboratory personnel verify that the samples are colder than 6°C upon receipt. Each delivery is accompanied by a chain of custody that is filled out by the sampler and signed by the laboratory. The local laboratory will add 2 mL of sulfuric acid to preserve the sample down to less than a pH of 2 within 48 hours of the initial grab sample. It will then be shipped overnight to their lab in Southern California and analyzed accordingly. Once preserved, nitrate has a hold time of 28 days.

Analytical methods and field measurements

The standard operating procedures to be used are attached to this document. Other than flow measurement, which will be gathered from the groundwater well and from the flow entering the biofilter, and calculated for the flow contributed from the channel, no field samples or data will be collected, either grab or continuous. Once the sample is at the laboratory, laboratory personnel will use EPA method 353.1 for nitrate and nitrate, EPA method 350.1 for ammonia (total only, not speciated), and EPA method 351.2 for Kjeldahl nitrogen. The addition of Kjeldahl nitrogen, nitrate, and nitrate equal total nitrogen. Reporting limits and method detection limits are defined in the commercial laboratory's special project method summary. Cadmium reduction for the analysis of nitrate results in a cadmium waste product. This waste product will be collected, stored and disposed of using Clinical Laboratories San Bernardino procedures for waste disposal. The laboratory shall turn the samples around in their standard 10 business days. No non-standard methods shall be used.

Parameter	Analytical Method	Reporting Limit[2]	Units
Discharge Flow or Volume	Field Measure	---	gpm
Nitrate (as N)	EPA 353.1	0.4	mg/L
Nitrite (as N)	EPA 353.1	400	ug/L
Total Ammonia as N	EPA 350.1	0.145	mg/L
Kjehldahl Nitrogen	EPA 351.2	1.0	mg/L

Quality Control

The commercial laboratory will follow its quality control, including blanks, spikes, and duplicates according to the requirements specified in the respective analytical methods. Field duplicates will be taken on 5% of the samples per SWAMP requirements. Please see the table in the appendices named Santa Maria special Project Method Summary. If control limits are exceeded, the sample will be flagged or rejected as appropriate. The commercial laboratory's special project method summary and individual analyte methods are attached.

Analyte	Accuracy	Precision	Completeness
	Measured through certified reference material, laboratory control samples	Measured through lab duplicates, matrix spike duplicates; field duplicates	Assess percent of data successfully measured
Nitrate-Nitrite	80 – 120%	RPD<25%	90%
Ammonia	80 – 120%	RPD<25%	90%
Kjehldahl Nitrogen	80 – 120%	RPD<25%	90%

Accuracy For laboratory measures, accuracy is determined by lab matrix spikes, certified reference material, and laboratory control samples. Data should be flagged as appropriate when RPD exceeds objectives. Use the following formula to calculate RPD between the two samples:

$$RPD = \frac{[A - B]}{B} \times 100\%$$

Where: RPD = the relative percent difference
A = the instrument measurement after sampling
B= the instrument measurement before sampling

Precision measurements are typically determined by the resolution of the instrument, and by evaluation of field and laboratory duplicates (or splits). Field duplicates account

for both precision of sampling techniques, laboratory analysis, as well as environmental variability. Field splits consist of two aliquots from the same composite sample, and field duplicates will consist of two grab samples collected in rapid succession. Laboratory duplicates are used to evaluate precision of the laboratory process. RPD is expressed as:

$$RPD = \frac{[D - P]}{P} \times 100\%$$

Where: RPD = the relative percent difference
D = the measured value in the duplicate sample
P= the measured value of the primary sample

Recovery measurements are determined by laboratory spiking of a replicate sample with a known concentration of the analyte (the parameter being analyzed). The target level of addition should be at least twice the original sample concentration.

Completeness is the number of analyses generating useable data for each analysis divided by the number of samples collected for that analysis. So for example, if one bottle was broken in transit, and 10 samples were collected in total, the completeness is 9/10 X 100 = 90%.

Instrument/equipment Testing, Inspection, and Maintenance

There are no field equipment needing periodic maintenance for this project. The commercial laboratory will follow its own inspection and maintenance program as needed. If sample results fall within QA/QC limits, then the city will assume that the laboratory equipment is being inspected and maintained properly.

Instrumentation/equipment calibration frequency

There are no field equipment needing calibration for this project. The commercial laboratory will follow its own calibration program if needed. If sample results fall within QA/QC limits, then the city will assume that the laboratory equipment is being calibrated properly.

Inspection/acceptance for Supplies and Consumables

There are no field supplies or consumables needed for this project, except sample bottles, which will be provided by the commercial laboratory.

Nondirect Measurements

No nondirect measurements will be used. CCAMP data may be used in the assessment. CCAMP data meets full SWAMP quality assurance standards.

Data Management

All data from this project, including chains of custody and sample results, will be stored in hard file in a file folder located at 2065 East Main Street, Santa Maria. Results from sampling will be entered into a spreadsheet, in a format that is consistent with CEDEN so that the data can be graphed. There will be no continuous monitoring data collected. City water systems operators will be responsible for collecting the samples per the Standard Operating Procedure, and the Water Resources Manager will be responsible for filing, compiling, and entering the data into CEDEN. Data will be submitted electronically to the Grant Manager in Quarterly Reports.

Assessment and Oversight

Water Resources Manager will be responsible for continually assessing the program and ensuring that all elements of the program meet the purpose for the grant. During construction, a city inspector will verify conformance of the construction to the drawings and to city specifications. Any variance will be reported to the project manager, who is the Water Resources Manager. Water Resources Manager will be responsible for following up for corrective actions.

Reports to Management

Data will be graphed quarterly until the development of the final report. The reports will be prepared by the Water Resources Manager and submitted to the Utilities Director and to the Business Services Manager of the City of Santa Maria, Utilities Department, on the last date of each quarter (i.e March 31, June 30, September 30, and December 31).

Data validation and usability

Data meeting the commercial laboratory's QA/QC program will be used. Data not meeting the commercial lab's QA/QC will be evaluated for inclusion on a case by case basis. Please see the table in the appendices named Santa Maria special Project Method Summary.

Verification and Validation Methods

Data will be validated by comparing the individual species of nitrogen with the total nitrogen number to make sure that they make sense. It is the responsibility of the Water Resources Manager to make sure they add up correctly, the chain of custody forms are filled out completely, that data entries do not contain typos, that outliers are evaluated and explained, and that the QA/QC data is acceptable and meets the necessary criteria. Any data that cannot be verified or validated will be thrown out and a new sample will be

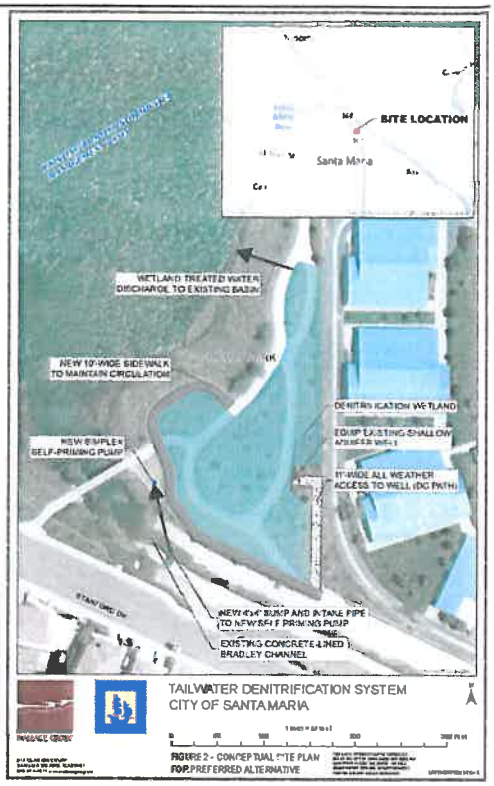
collected and analyzed and validated by comparing to the method quality objectives. Please see the table in the appendices named Santa Maria special Project Method Summary.

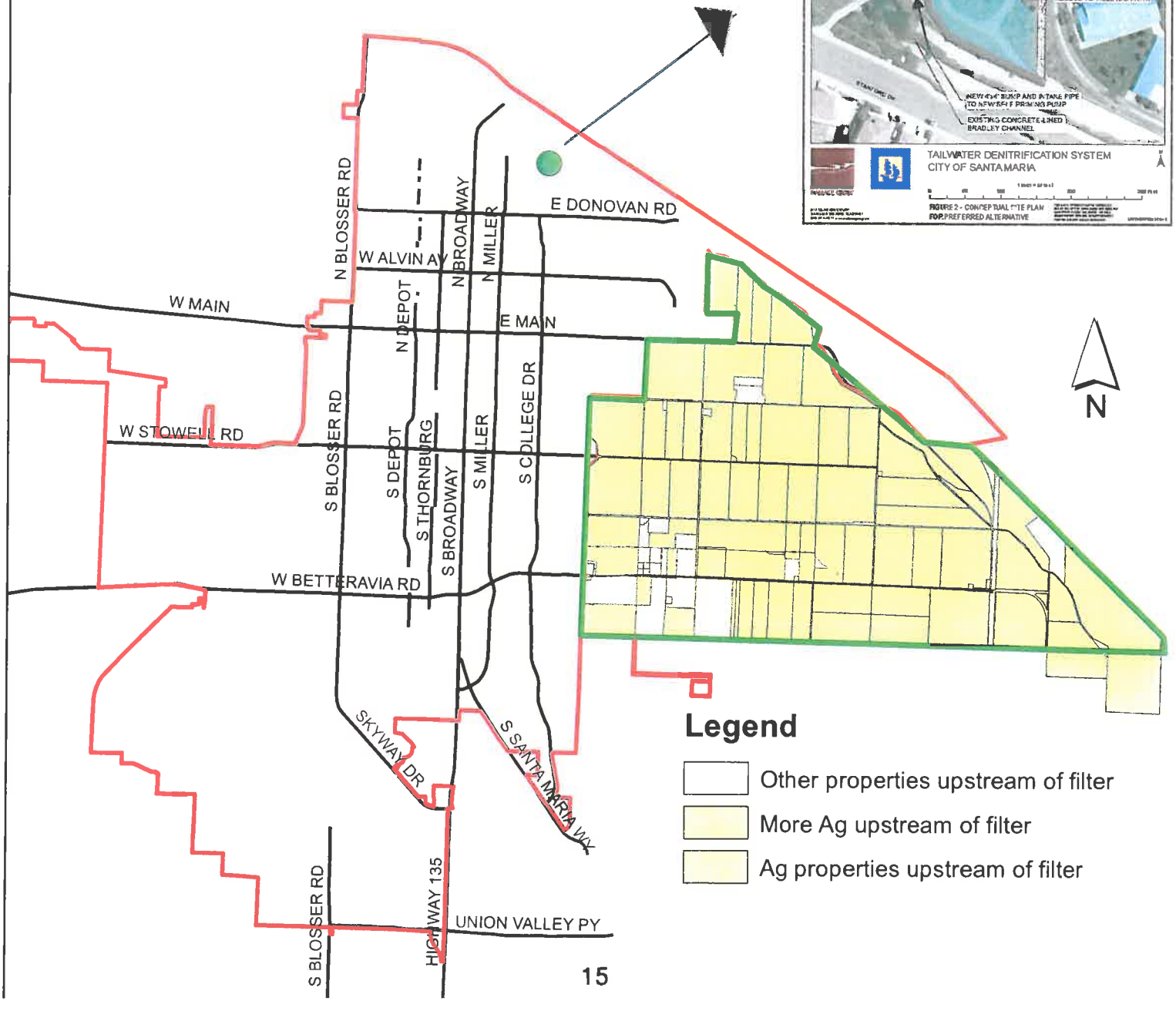
Reconciliation with User Requirements

The anticipated outcome of this project is to achieve a biofilter effluent of less than 10 mg/L of nitrate as N. If the nitrate exceeds 10 mg/L, then the biofilter operation, the city will evaluate the biofilter to determine if parameters can be adjusted to achieve the desired goal. In addition, the data will be able to show whether the desired outcome can be achieved under different operating parameters, such as ambient air temperature, incoming nitrate, or operational mode (steady state versus batch operation).

Appendix 1
Jim May Park Agriculture Tailwater Treatment
Grant # 14 – 475 – 553
Proposition 84 Agricultural Water Quality Grant

The City recently secured a Proposition 84 grant of $1,250,000 from the State Water Resources Control Board for an Agriculture Tailwater Treatment Project. This project will involve treatment of agricultural tailwater to reduce nitrite/nitrate, total suspended solids and other pollutants to meet Basin Plan objectives. A woodchip biofilter will be installed at Jim May Park to treat water from Bradley Channel which drains 5700 acres of agricultural land and 913 acres of urban land.





	Department Utilities	**Author** S. Sweeney	Santa Maria All-America City
	Division Water Resources	**Revision** 1	
	Group Water Production	**Effective Date** 12/23/15	

Sampling Protocol-Biofilter

Purpose: The purpose of the biweekly biofilter system sampling is to meet the monitoring requirements of the Proposition 84 grant funding and to determine the effectiveness of the biofilter at removing nitrogen.

Step	Action
1	Secure an ice chest, 3 blue ice blocks, a squirt bottle with D.I. water, and a minimum of six ½ pint plastic bottles.
2	Secure a clipboard with Chain of Custody (COC).
3	Drive to the sample site. Fill two bottles from each sample location. The sample locations are upstream of the biofilter, downstream of the biofilter, and the groundwater well if running. Open the sample tap to establish flow.
4	Fill each plastic bottle to the neck, cap it, and place it in the ice chest from each of the three possible sample ports.
5	Record the time and sample number on the Chain of Custody, and fill out the labels on the outside of the bottles. Label one bottle from each sampling location for nitrite and nitrate, and label the other bottle for ammonia and Kjeldahl nitrogen
6	Once back in the laboratory, place samples in the refrigerator or in an ice chest with ice.
7	Make sure that the COC is filled out properly. Have the sample analyzed for ammonia, nitrate, and total nitrogen. Sign your name. Make notes on the COC if it was raining or if you observed any other unusual conditions. Put the COC on the lab desk.
8	Make sure that the samples are received by the commercial laboratory within 48 hours of sampling so that the nitrite and nitrate sample can be acidified before the end of 48 hours.
9	
10	
11	
12	

Santa Maria Special Project Method Summary

Analysis	Method	Units	MDL	DLR	DLR Recovery	LCS Recovery	Matrix Spike Recovery
Nitrate-N	EPA 353.2	mg/L	0.021	0.40	50 - 150 %	90 - 110 %	90 - 110 %
Nitrite-N	EPA 353.2	ug/L	27	400	50 - 150 %	90 - 110 %	90 - 110 %
Ammonia-N	EPA 350.1	mg/L	0.15	0.50	50 - 150 %	90 - 110 %	90 - 110 %
Total Kjeldahl-N	EPA 351.2	mg/L	0.46	1.0	50 - 150 %	90 - 110 %	90 - 110 %

Units: mg/L - milligrams per liter (PPM); ug/L - micrograms per liter (PPB)
MDL: Method Detection Limit
DLR: Detection Limit for Reporting
LCS: Lab Control Standard - Known amount of analyte to check for analytical accuracy
Matrix Spike: Known amount of analyte added to a real world sample to check for analytical interference
Recovery: Allowable deviation from the true value

Total Nitrogen: Mathmatical sum of Nitrate-N, Nitrite-N, and Total Kjeldahl-N results

CLINICAL LABORATORY OF SAN BERNARDINO, Inc.

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF AMMONIA BY DISTILLATION AND COLORIMETRY

1. SCOPE AND APPLICATION:

1.1 This method is applicable for surface, drinking, treated, waste and ground water.

1.2 The applicable range is 0.01-50 mg/L NH_3-N. Higher concentrations can be determined by sample dilution.

2. REPORTING LIMIT:

2.1 DLR is 0.5 mg/L for Ammonia as N and 0.6 mg/L for Ammonia as NH_3.

3. APPLICABLE MATRIX AND MATRICES:

3.1 Please refer to Section 1.1.

4. SUMMARY OF THE METHOD:

4.1 A sample of water is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is distilled into a solution of boric acid. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color is intensified with sodium nitroprusside and measure colorimetrically at 630 nm.

5. DEFINITIONS:

5.1 Batch – consists of twenty samples and must contain a LCS, MBLK, MS1, MS2, and a CCV every 10 samples.

5.2 Calibration Standard (CAL) – A series of standards prepared from the primary standard to calibrate tests.

5.3 Continuing Calibration Verification (CCV) – A midpoint primary source calibration standard run at the beginning and end of each analytical batch; used to verify the calibration.

5.4 Detection Limit for Reporting (DLR) – A practical limit that can be reported for the method which is usually 2 times higher or more than the MDL.

5.5 Flow Injection Analysis (FIA) – References to the Seal equipment.

5.6 Initial Calibration Verification (ICV) – A midpoint primary source calibration standard run at the end of every calibration; used to verify the calibration.

5.7 Laboratory Control Sample (LCS) – A control sample to check method performance

5.8 Linear Calibration Range (LCR) – The concentration over which the test is linear.

5.9 Matrix Spike (MS) – A sample that is spiked at mid-level concentration to check matrix effect of samples; it is also to determine precision and accuracy of this test.

5.10 Method Blank (MBLK) – Run every 20 samples used as a control sample to confirm a clean system free from interference.

5.11 Method Detection Limit (MDL) – Method Detection limit is at 99% confidence limit that the analyte concentration will be greater than zero.

5.12 Primary Dilution Standard (PDS) – A standard from a certified source used to calibrate test or develop a calibration curve.

5.13 Secondary Dilution Standard (SDS) – A standard from a certified source used to prepare the LCS, MS.

6. CONTAMINATION AND INTERFERENCES:

6.1 There can be potential contamination and interferences from using reagents that are not analytical grade. Potential interferences may come from glassware and containers.

6.2 Cyanate, which may be encountered in certain wastes, will hydrolyze to form ammonia.

6.3 Residual chlorine must be removed by pre-treatment with sodium thiosulfate.

7. APPARATUS AND MATERIALS:

7.1 Analytical Balance that weighs 0.0001 g.

7.2 100 mL Volumetric Flasks, Class A.

7.3 A Kontes Midi-Vap 2000 Distillation system (Model 47190-2000).

7.4 Auto Analyzer 3 High resolution.

7.5 2 channel manifold high resolution (HR) Digital Colorimeter.

7.6 Dell precision computer with 6.04 software and Dell 1720 Printer.

7.7 pH paper (for 9.5, use pH paper range 7-14 with 0.5 increments).

7.8 190 cm sample loop.

7.9 50 mL graduated cylinder.

7.10 180 Position auto-sampler.

7.11 Injection module.

7.12 13 x 100 mm glass culture tubes.

8. REAGENTS AND STANDARDS:

8.1 Reagent grade de-ionized water, Nanopure or equivalent.

8.2 Sodium Hydroxide 1 N: 40 g of Sodium Hydroxide in 1 Liter.

8.3 Borate buffer dissolve 9.5 of sodium borate decahydrate and 88 mL of 1 N NaOH in 1 Liter of water.

8.4 Boric Acid – 20 g of Boric Acid in 1 Liter of reagent water.

8.5 Sodium Phenolate: Mix 16.6 g of crystalline phenol and 6.4 g of NaOH with 100 mL of reagent water. Cool and make up to a final volume of 200 mL.

8.6 Sodium Hypochlorite: Add 26.25 mL of 6% hypochlorite solution and bring to up to 100 mL volume with reagent water.

8.7 Sodium Nitroprusside: Dissolve 32g of disodium EDTA and 0.4g of NaOH in about 600 ml of DI water. Then dissolve 0.18 g sodium nitroprusside and dilute to 1 liter with DI water. Mix thoroughly and add 3 ml of Brij-35 solution.

9. SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE:

9.1 Samples are collected in plastic bottles. The holding time is 28 days.

9.2 Samples must be preserved with H_2SO_4 to a pH < 2 and cooled to $4\pm2^{\circ}C$.

10. QUALITY CONTROL:

10.1 Each batch is 20 samples and contains an LCS, MBLK. CCV and MS are run every 10 samples. Each run contains a DLR. MBLK must be less than 0.50 mg/L. The calibration curve correlation coefficient must be > 0.995.

10.2 The LCS concentration is 25 mg/L and must be within 90 – 110% acceptance. The MS concentration is 15 mg/L and must be within 90 – 110% acceptance.

11. CALIBRATION AND STANDARDIZATION:

11.1 Standardization is achieved using Auto Analyzer 3 High resolution 6.04 software.

11.2 All standard curves are linear and will run with a correlation coefficient of 0.995 or better for all ammonia analysis. Failure at this point will require a re-standardization or preparation of new standards.

11.3 All data stored with the Auto Analyzer 3 High resolution 6.04 software provides for imbedding of the calibration curve raw data. The electronic data file including the chromatograms can be retrieved and reviewed when needed.

11.4 Prepare calibration standards at concentrations of 0, 0.5, 5, 25, and 50 mg/L.

11.5 Load into auto-sampler after the instrument has properly warmed up and a stable baseline is obtained. Refer to Section 12 for instrument set-up.

11.6 Verify the calibration curve with an initial calibration verification (ICV) check. The ICV must be within 90 – 110% acceptance.

11.7 Use continuing calibration verification (CCV) standards at the beginning and end of every 10 samples to verify the calibration curve which must be within 90 – 110% acceptance.

12. PROCEDURE:

Part A Standard Distillation:

12.1 Set up the Midi-Vap 2000 Distillation Systems Colorimeter according to manufacturer's instructions. Connect part A and part B of the distillation flasks to the Midi-Vap 2000. Place anti-siphon glass on top of the distillation flask with the 125 mL Erlenmeyer flask on the bottom to collect the sample.

12.2 Ensure the Coolflow CFT-33 is filled with enough de-ionized water. Turn on the Coolflow and wait for the temperature to reach 4°C.

12.3 Turn on the Midi-Vap 2000 and set timer to 120 minutes with a temperature at 200°C.

12.4 Turn on condenser water and prepare a blank sample to clean out the system.

12.5 Prepare calibration standard and other QC standards as stated in Table 1.

12.6 Measure 50 mL of each standard into a graduated cylinder and transfer solution into the distillation flask. Add 2.5 mL of borate buffer.

12.7 Verify pH. The pH should be around 9.5. Adjust pH to 9.5 with 1 N NaOH if needed.

12.8 Quickly add boiling chips to each distillation flask.

12.9 In the Erlenmeyer flask add 5 mL of boric buffer.

12.10 The condenser tip must extend below the level of the boric buffer solution. Turn on Midi-Vap 2000 and distil for 120 minutes at 200°C. After distillation bring volume up to 50 mL.

Part B Sample Distillation:

12.11 Measure 50 mL each sample using a graduated cylinder and place into a distillation flask. Add 2.5 mL borate buffer to each sample.

12.12 Add 1 N Sodium Hydroxide solution as needed until the pH is 9.5.

12.13 Record the pH of the sample in the distillation logbook.

12.14 Pour solution into distillation flask and allow each sample to distillate.

12.15 Quickly add boiling chips to each distillation flask.

12.16 In the Erlenmeyer flask add 5 mL of 2% boric acid.

12.17 The condenser tip must extend below the level of the boric acid solution.

12.18 For MS preparation: Measure 50 mL of sample into a 50 mL volumetric flask. Add spike at 750 µL of SDS into volumetric flask and bring to volume with sample. Transfer solution into an Erlenmeyer flask. Add enough 1 N NaOH to bring pH to 9.5. Transfer solution into distillation flask. Repeat steps 12.13-12.17.

12.19 The temperature for ammonia distillation should be adjusted to 200°C for 121 minutes.

12.20 It takes approximately 10 minutes for distillation to reach equilibrium and requires approximately 2 hours total run time to recover 50 mL per station. After distillation bring each sample to a 50 mL volume.

Instrument Setup Procedure:

12.21 Ensure the 630 nm filters are in the colorimeter for NH_3-N method.

12.22 Place all feed lines into de-ionized water containing Brij-35 and switch on all Auto-analyzer 3 modules. The valve for the column must be in the closed position.

12.23 To start the pump, close the pump platen. Set the power switch located on the side of the pump to position 1, which is on. Set the red switch on top of the pump to position RUN and the black switch to position normal. The rollers will now start rotating.

12.24 Check bubble pattern in all lines, especially the flow cell waste line.

12.25 Check the Water baseline by starting charting option in AACE to display charts with the channel readings. The water baseline should be stable and flat.

12.26 Place the reagent lines from the wash receptacle into the reagent containers. Check that the bubble pattern is still okay with reagents; baseline should be stable and flat.

12.27 Select set-up and select analysis. In analysis select NH_3-N method. Select new run to enter the sample information. Select O.K. to save after all the samples have been entered. Name the sequence by the date started (year, month, day).

12.28 Load the standards and samples into the tubes according to sequence. Start the run, select the date of the run for the sequence and select O.K.

12.29 Check to see that LCS is running within the true value of +/- 10%. When the analysis is complete, remove the pump reagent lines and run reagent water through the system to clean the lines. If needed the lines can be cleaned with 1 N HCl and then rinsed with reagent water. Turn off the pump and modules. Release the pump tube cassettes.

13. CALCULATIONS:

13.1 Instrument software calculates results based on integration parameters.

14. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA:

14.1 Inform supervisor and notify QA/QC Manager for any non-conformance issues.

15. POLLUTION PREVENTION AND WASTE MANAGEMENT:

15.1 If samples are hazardous, dispose of after holding time in accordance with DOHS and EPA requirements.

16. REFERENCES:

16.1 EPA Method 350.1. "Determination of Ammonia Nitrogen by Semi-Automated Colorimetry." U.S. Environmental Protection Agency. (1993). <http://www.epa.gov/epahome/index/>

16.2 Method MT G145-95 Rev.3. "Ammonia in Waters." Auto Analyzer 3

17. TABLES, DIAGRAMS, FLOW CHARTS, Etc:

17.1 Control Charts used to monitor performance.

17.2 Table 1: Standard Preparation

Standard Name	Initial Conc. (ppm)	Amt. Added (mL)	Final Conc. (ppm)	Final Volume (mL)

Cal-1	1000	25	50	500
Cal-2	1000	25	25	1000
Cal-3	25 (PDS)	100	5.0	500
Cal-4	25 (PDS)	10	0.5	500
Cal-5	0	0	0.0	500
DLR*	1000	0.5	0.5	1000
LCS/*	1000	25	25	1000
MS*	1000	15	15	1000
ICV/ CCV	1000	25	25	1000

*Uses a secondary source standard (SDS) for preparation.

18. TRAINING and QUALIFICATION VERIFICATION:

18.1 Signature of analyst and trainer on file with qualifying card.

19. HEALTH and SAFETY:

19.1 Proper safety procedures should be used for handling chemicals used in this test. The method analytes used in this test are classified as hazardous and appropriate safety procedures implemented such as respirator, lab coat, rubber gloves and glasses.

19.3 MSDS on file for chemical reference as needed.

Department: Inorganics

Method Approved By:

Khurshid Ahmed
Department Supervisor

Date: _____

Bob Glaubig
Laboratory Director

Date: _____

Alex Popa
QA/QC Manager

Date: _____

CLINICAL LABORATORY OF SAN BERNARDINO, Inc.

STANDARD OPERATING PROCEDURE FOR NITROGEN, NITRATE-NITRITE (COLORIMETRIC, AUTOMATED, CADMIUM REDUCTION)

1. SCOPE AND APPLICATION:

1.1 This method covers the determination of nitrite alone or nitrite plus nitrate in drinking, ground, surface, domestic water, and industrial wastes. All standard curves are linear.

1.2 The applicable range is 0.05 – 20.0 mg/L Nitrate-Nitrite nitrogen. The range may be extended with sample dilution.

2. REPORTING LIMIT:

2.1 The reporting limit for NO_3 as N is 0.4 mg/L and NO_2 as N is 400 µg/L, and 50 µg/L (low-level).

3. APPLICABLE MATRIX AND MATRICES:

3.1 Not Applicable.

4. SUMMARY OF METHOD:

4.1 NO_3 is reduced to nitrite by passing a filtered sample through a column containing granulated copper-cadmium. The NO_2 (that was originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-1(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically at 520 nm on the FIA. Both acidified and un-acidified samples can be analyzed without further manual pH adjustment (per attached Exhibit M2, 2010 Inspection Response).

5. DEFINITIONS:

5.1 Calibration Blank (CB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes run at the end of every calibration.

5.2 Calibration Standards (CAL) – A series of standards that will be used to calibrate an instrument with a primary dilution standard (PDS).

5.3 Instrument Performance Check Solution (IPC) – A solution of one or more method analytes to evaluate the performance of the instrument with respect to a defined set of criteria.

5.4 Detection Limit for Reporting (DLR) – A practical limit that can be reported for the method which is usually 3 times higher or more than the MDL.

5.5 Flow Injection Analysis (FIA) – colorimetric procedure.

5.6 Laboratory Control Sample (LCS) – This is prepared from a spiked reagent water sample prepared at mid-range of the calibration standards. This is prepared from a second source standard (SDS).

5.7 Matrix Spike (MS) – A sample is selected and spiked with a second source standard (SDS) at mid-level concentration.

5.8 Method Blank (MBLK) – A sample of reagent water that is treated as a sample in the analytical test and is a control for system cleanliness.

5.9 Method Detection Limit (MDL) – The lowest value this method can detect based on empirical, statistical data.

5.10 Milligrams Nitrogen per Liter (mg N/L).

5.11 Primary Dilution Standard (PDS) – A standard that is used to make a series of calibration standards and IPC.

5.12 Parts per million (ppm).

5.13 Secondary Dilution Standard (SDS) – A sample of standard from a second source that is used to prepare the LCS and MS standards.

6. CONTAMINATION AND INTERFERENCES:

6.1 Samples to be run should be free of suspended matter as this will clog the column and shift window timing. Since nitrate and nitrite are found in a soluble state, samples may be pre-filtered.

6.2 Concentration of iron, copper or other metals above several milligrams per liter lower reduction efficiency. EDTA is added to the samples to eliminate this interference.

6.3 Oil and grease will coat the cadmium surface; it will cause interference. It is eliminated by pre-extracting the sample with an organic solvent.

6.4 Colored samples, which absorb at 520 nm interference, should be filtered.

7. APPARATUS AND MATERIALS:

7.1 Auto-Analyzer 3 High resolution.

7.2 180 Position Autosampler.

7.3 Multi-channel Proportion Pump.

7.4 Injection Module.

7.5 Two channel/manifold High resolution (HR) Digital Colorimeter.

7.6 10 mm, 30 mm, and 50 mm flow cells.

7.7 520 nm interference filters.

7.8 18 cm sample loop.

7.9 Cadmium column (HACH Catalog no. 5023712).

7.10 Dell precision Computer with 6.04 software.

7.11 Dell Color Monitor.

7.12 Dell 1720 printer.

7.13 VWR disposable syringes with 0.45 µm filters.

7.14 Volumetric Flasks.

7.15 Pipette with disposable sterile pipette tips.

7.16 13 x 100 mm glass culture tubes.

7.17 Brij-35

8. REAGENTS AND STANDARDS:

8.1 De-ionized water.

8.2 15N Sodium Hydroxide.

8.2.1 Add 150 g NaOH very slowly to 250 mL of DI water, swirl until dissolved.

8.3 Ammonium Chloride Buffer

8.3.1 Dissolve 170 g of ammonium chloride (NH_4Cl) and 0.2 g of disodium ethylenediamine tetracetate dihydrate (EDTA), ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$) in approximately 1600 mL of distilled water. Add 15N NaOH to adjust pH to 8.5 $\pm$ 0.1 and dilute to 2 liters. Add 1.0 mL of BriJ-35. Replace weekly.

8.4 Color Reagent

8.4.1 To approximately 1600 mL of distilled water add 148 mL of 85% phosphoric acid (H_3PO_4). Add 59.2 g of sulfanilamide and 3.0 g N-1-Naphthylenediamine dihydrochloride ($C_{10}H_7NHCH_2CH_2NH_2 \cdot 2HCL$) dissolve completely, dilute to two liters. Add 1.0 mL of Brij-35 and store in a dark bottle. This reagent is stable for one month. Degas with helium.

8.5 Stock Nitrite Standard (1000 ppm N/L as N)

8.5.1 Order from ERA Cat. No. 990. All standards (calibration and QC) must be prepared fresh daily from the stock nitrite standard. The expiration of working stock solutions will be identical the expiration date of purchased stock standards.

8.6 Stock Nitrate Standard (1000 ppm N/L as N)

8.6.1 Order from ERA Cat. No. 991.

8.7 Stock Anion Standard (100 ppm NO_2 as N and 2500 ppm NO_3).

Calibration Standards

8.8 Nitrate as N calibration standards are prepared by diluting stock solution and PDS into a 1L volumetric flask according to the following table.

Standard Name	Final Conc.	(mL) used	Initial Conc.	Final Volume
Std-1	20 ppm	10	1000 ppm	500 mL
Std-2	10 ppm	5	1000 ppm	500 mL
IPC	10 ppm	5	1000 ppm	500 mL
Std-3	5 ppm	5	1000 ppm	1000 mL
Std-4	2.5 ppm	5	1000 ppm	2 L
Std-5	0.4 ppm	40	5 ppm	500 mL
DLR*	0.4 ppm	0.2	1000 ppm	500 mL

*DLR is made from a secondary source dilution standard (SDS).

8.9 Nitrite as N calibration standards are prepared by diluting stock solution and PDS into a volumetric flask according to the following table.

Standard Name	Final Conc.	(mL) used	Initial Conc.	Final Volume
Std-5ppm	5 ppm	2.5	1000 ppm	500 mL
Std-1	2 ppm	1	1000 ppm	500 mL
Std-2	1 ppm	100	5 ppm	500 mL
IPC	1 ppm	100	5 ppm	500 mL
Std-3	0.5 ppm	50	5 ppm	500 mL
Std-4	0.1 ppm	10	5 ppm	500 mL
Std-5	0.05 ppm	5	5 ppm	500 mL

DLR*	0.4 ppm	0.2	1000 ppm	500 mL
DLR (low level)	0.05 ppm	25	0.4 ppm	500 mL

*DLR is made from a secondary source dilution standard (SDS).

8.10 Nitrite as N and Nitrate LCS, MS are prepared by diluting a secondary source anion stock solution PDS in a volumetric flask according to the following table.

Standard Name	Final Conc. (µg/mL)	Amt. used	Initial Conc. (µg/mL)	Final Volume (mL)
MS (NO_2-N)	0.5	250 µL	100	50
MS (NO_3)	12.5	500 µL	2500	100
LCS (NO_2-N)	1.0	2.0 mL	1000	2000
LCS (NO_3)	25	20 mL	2500	2000

8.11 All standards are placed into the auto-sampler.

9. SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE:

9.1 Samples not analyzed within 48 hours should be preserved with H_2SO_4 to below pH 2 and cooled to 4°C.

9.2 Store all standards in a cool environment.

9.3 Store the Color reagent in a cool, dark environment.

9.4 The holding time is 28 days for acidified samples.

10. QUALITY CONTROL:

10.1 Each set of 10 samples will include an IPC, LCS, MBLK, Matrix Spike.

10.2 Run IPC, LCS and MBLK at the beginning and the end of analysis.

10.3 The MS recovery must be 90 – 110%.

10.4 The LCS, IPC recovery must be 90 – 110%.

10.5 The DLR recovery must be 50 – 150%.

10.6 The MBLK must be < 0.4 mg/L.

10.7 The software performs a linear regression on the standards.

10.8 The correlation coefficient for this regression must be 0.995 or higher.

10.9 Compare the results of the IPC NO_2 –N (1000 µg/L) standard to the results of the 1000µg/L NO3-N standard; both analyzed using the NO_3-N calibration standards. Recovery should be 80-120 % (per manufacturer's recommendation).

11. CALIBRATION AND STANDARDIZATION:

11.1 Prepare a series of five standards covering the desired range, and a blank by diluting suitable volumes of standard Nitrate and Nitrite solution as mentioned in Section 8.8 and 8.9.

11.2 Set-up manifold. Care should be taken not to introduce air into the reduction column.

11.3 Place standards in the sampler in order of decreasing concentration.

11.4 Prepare standard curve by plotting instrument response against concentration value.

11.5 After the calibration has been established, it must be verified by the analysis of a suitable quality control sample. The measurement must be within $\pm$ 10% of established value.

11.6 Condition new column by pumping through the sample line 20 mg NO_3-N/L for 10 minutes and 2.0 mg NO_2-N/L for 20 minutes. Subsequently wash the column with reagents for 20 minutes.

12. PROCEDURE:

Automated Colorimetric procedure set-up on auto-analyzer 3 high resolution.

12.1 Ensure the 520 nm filters are in the colorimeter for Nitrogen NO_3-NO_2 method.

12.2 Place all feed lines into de-ionized water containing Brij-35 and switch on all Auto-analyzer 3 modules. The valve for the column must be in the closed position.

12.3 To start the pump, close the pump platen. Set the power switch located on the side of the pump to position 1, which is on. Set the red switch on top of the pump to position RUN and the black switch to position normal. The rollers will now start rotating.

12.4 Check bubble pattern in all lines, especially the flow cell waste line.

12.5 Check the Water baseline by starting charting option in AACE to display charts with the channel readings. The water baseline should be stable and flat.

12.6 Place the reagent lines from the wash receptacle into the reagent containers. Check that the bubble pattern is still okay with reagents and baseline should be stable and flat.

12.7 Open the valve for column so that buffer solution can go in.

12.8 Select set-up and select analysis. In analysis select NO_3-NO_2 method. Select new run to enter the sample information. Select O.K. to save after all the samples have been entered. Name the sequence by the date started (year, month, day).

12.9 Load the standards and samples into the tubes according to sequence.

12.10 Start the run and select the date of the run for the sequence and select O.K.

12.11 Check the standardization and the cadmium column efficiency before continuing the run.

12.12 Verify the calibration curve with Instrument Performance Check (IPC). The IPC must be within 90 – 110% acceptance. Then after every ten samples and at the end of analysis.

12.13 Follow the run-log sequence and print data reports when done.

13. CALCULATIONS:

13.1 Data analysis is calculated with Seal 6.04 Software.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT:

14.1 A major source of pollution used in this method is the use of Cadmium.

14.2 All cadmium after use will be collected and stored for disposal.

14.3 Use Clinical Laboratory of San Bernardino, Inc. procedures for Waste Disposal.

15. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA:

15.1 The correlation coefficient, (r), value must be at least 0.995 at all times.

15.2 The MS must be within 90 – 110%. The sample chosen for MS can interfere with the analyte of interest, in which case the matrix interference must be noted on the run log.

15.3 The LCS, IPC must be within 90 – 110% acceptance. The Cadmium Reduction efficiency must be at 80 – 120%. The DLR must be within 50 – 150% recovery, the MBLK must be < 0.4 mg/L.

15.4 See QA/QC manager for non-conformance issues.

16. REFERENCES:

16.1 USEPA Method 353.2

16.1.1 EPA (August 1993) Method 353.2 (colorimetric automated, cadmium reduction).

16.1.2 Seals Auto-analyzer 3 High resolution, method MB 7-31 EN-02.

16.1.3 EPA Appendix B to part 136 – Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11, 40 CFR Ch. 1 d (7-1-94 edition).

16.1.4 1030c. Precision using duplicates, Standard Methods for the Examination of Water and Wastewater, 19th Ed. 1992, American Public Health Association, 1015 Fifteenth Street, NW Washington, DC 20005.

17. TABLES, DIAGRAMS, FLOW CHARTS, Etc:

17.1 Not Applicable.

18. TRAINING AND QUALIFICATION VERIFICATION:

18.1 Signature of analyst and trainer on file with data.

19. HEALTH AND SAFETY:

19.1 This method uses Cadmium granules. Cadmium is toxic and carcinogenic. Wear protective eyewear, latex gloves and lab coat when copperizing granules. MSDSs are on file for Chemical reference as needed.

Department: Inorganics

Method Approved By:

_____
Khurshid Ahmed
Department Supervisor

Date: _____

_____
Bob Glaubig
Laboratory Director

Date: _____

_____
Alex Popa
QA/QC Manager

Date: _____

Clinical Laboratory of San Bernardino, Inc.

Standard Operating Procedure for the Determination of Total Kjeldahl Nitrogen by Auto Analyzer 3

1. SCOPE AND APPLICATION:

1.1 The purpose of this method is to determine Total Kjeldahl Nitrogen content in drinking, surface, domestic and industrial waters. The procedure converts nitrogen components of biological origin such as aminoacids, proteins and peptides to ammonia.

2. REPORTING LIMIT:

2.1 The Detection Limit for Reporting (DLR) is 1.0 mg/L of N for water samples. DLR is compound, instrument, and matrix dependent. We are currently reporting at the state DLR levels. The MDL, as determined in March 2014, is 0.46 mg/L.

3. APPLICABLE MATRIX AND MATRICES:

3.1 Please refer to Section 1.1.

4. SUMMARY OF METHOD:

4.1 The sample is heated in a digestion block with digestion solution for three and a half hours. The residue is cooled, diluted to 20 mL and placed on an auto-analyzer for ammonia determination.

5. DEFINITIONS:

5.1 Batch – consists of twenty samples and must contain a LCS, MBLK, MS and an opening and closing CCV.

5.2 Continuing Calibration Verification (CCV) – A midpoint primary source calibration standard run at the beginning and end of an analytical batch used to verify the calibration.

5.3 Calibration Standards (CAL) – A series of standards that will be used to calibrate an instrument made with a primary dilution standard (PDS).

5.4 Detection Limit for Reporting (DLR) – A practical limit that can be reported for the method which is usually 2 times higher or more than the MDL.

5.5 Flow Injection Analysis (FIA) – colorimetric procedure.

5.6 Initial Calibration Verification (ICV) – A midpoint primary source calibration standard run at the end of every calibration.

5.7 Laboratory Control Sample (LCS) – a sample of reagent water spiked with standard at mid-level of the calibration. This is prepared from a secondary source standard (SDS).

5.8 Matrix Spike (MS) – A sample is selected and spiked with a secondary source standard (SDS) at mid-level concentration. These samples are used for precision and accuracy data.

5.9 Method Blank (MBLK) – A sample of reagent water that is treated as a sample in the analytical test and is a control for system cleanness.

5.10 Method Detection Limit (MDL) – The lowest value this method can detect based on empirical and statistical data.

5.11 Milligrams of Nitrogen per Liter (mg N/L).

5.12 Primary Dilution Standard (PDS) – A standard that is used to make a series of calibration standards.

5.13 Second Dilution Standard (SDS) – A sample of standard from second source that is used to prepare the LCS, MS.

6. CONTAMINATION AND INTERFERENCES:

6.1 Ammonia or nitrogen containing compounds in the deionized water and reagents will interfere with the method.

6.2 Clean glassware is important to eliminate interferences.

7. APPARATUS AND MATERIALS:

7.1 Auto Analyzer 3 (AA3) High Resolution.

7.2 Two channel Manifold High Resolution (HR) Digital Colorimeter.

7.3 Westco Science digestions block with 75 mL glass tubes for digestion.

7.4 Teflon boiling chips for refluxing samples.

7.5 180 position autosampler.

7.6 Injection module.

7.7 Multi-channel Proportioning pump.

7.8 13x100 mm glass culture tubes.

7.9 660 nm interference filters.

7.10 Dell precision computer with the AA3 6.04 software.

7.11 Dell Color monitor.

7.12 Dell 1720 printer.

7.13 Brij-35.

8. REAGENTS AND STANDARDS:

8.1 Reagent water: nanopure water (ammonia free).

8.2 Sampler wash solution: add 80 mL of conc. H_2SO_4 to about 1800 mL of DI water. Dilute to 2000 mL with DI water and mix thoroughly.

8.3 Stock NaOH solution, 20%: dissolve 200 g of NaOH in about 700 mL of DI water. Cool to room temperature and dilute to 1000 mL with DI water.

8.4 Stock Buffer Solution, 0.5 m: dissolve 134g of disodium hydrogen phosphate heptahydrate in about 800 mL of DI water. Add 20g of NaOH, dilute to 1 L with DI water and mix thoroughly; keep closed.

8.5 Stock sodium potassium tartrate solution, 20%: dissolve 200 g of sodium potassium tartrate in about 800 mL of DI water. Dilute to 1 L with DI water and mix thoroughly; keep closed.

8.6 Working Buffer Solution: combine the reagents in the standard order: add 200 mL of stock sodium potassium tartrate solution, 20%, to 160 mL of stock buffer solution, 0.5 m, with swirling. Slowly while swirling, add 110 mL of NaOH solution 20%. Dilute to 1 L with DI water, add 2.0 mL of brij-35, 30% solution and mix thoroughly.

8.7 Sodium Salicylate/ Sodium Nitroprusside solution: dissolve 194 g of Sodium Salicylate and 0.4 g of Sodium Nitroprusside in about 600 mL of DI water. Dilute to 1 L with DI water and mix thoroughly.

8.8 Sodium Hypochlorite Solution: In 100 mL volumetric flask dilute 7.5 mL of 6% Hypochlorite to the mark with DI water and mix thoroughly. Prepare fresh daily.

9. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE:

9.1 Samples are collected in plastic containers.

9.2 Samples must be preserved with H_2SO_4 to a pH < 2.0.

9.3 Samples must be stored at 4°C.

9.4 Hold time for preserved samples is 28 days.

10. QUALITY CONTROL:

10.1 A Laboratory Control Sample (LCS), Matrix Spike (MS) are run with each group of 10 samples.

10.2 A detection Limit of Reporting (DLR) is run once at the beginning of each run.

10.3 A beginning and ending calibration verification check and Method Blank (MBLK) is run every 10 samples.

10.4 The concentration of LCS is 25 mg/L. The acceptable range is 90 – 110%.

10.5 The concentration of the ICV and CCV are 25 mg/L. The acceptable range is 90 – 110%.

10.6 The concentration of the MS is 25 mg/L. The acceptable range is 90 – 110%.

10.7 The concentration of DLR is 1 mg/L. The acceptable range is 50 – 150%.

10.8 Record all standards used in the standards preparation logbook and run logbook with reference to the chemical and standards inventory book.

10.9 All standards used in this method must be labeled with the standards preparation logbook number.

10.10 Record all deviations and non-conformances in the run logbook.

10.11 The correlation coefficient (R) on the calibration standards must be 0.995 or greater.

10.12 The method blank must be less than the DLR of 1.0 mg/L at all times.

10.13 This method is procedural as standards and samples are run the same.

11. CALIBRATION AND STANDARDIZATION:

11.1 A calibration curve is prepared with standards of 0.0, 1.0, 5.0, 10, 25, 40 and 50 mg/L. Please refer to Table 1 in Section 17 for reference.

11.2 Standardization is achieved using AA3 6.04 software.

11.3 All standard curves are linear and will run with a correlation coefficient of 0.995 or better for all TKN analyses. Failure at this point will require a re-standardization or preparation of new standards.

11.4 All data stored with the AA3 6.04 Software provides for imbedding of the calibration curve raw data. The electronic data file including the chromatograms can be retrieved and reviewed when needed.

11.5 Prepare calibration standards at concentration of 0, 1.0, 5.0, 10, 25, 40, and 50 mg/L.

11.6 Load into the auto-sampler after the instrument has properly warmed up and a stable baseline has been obtained. Refer to Section 12 for instrument set-up.

11.7 Prepare standard curve by plotting instrument response against concentration value.

11.8 Verify the calibration curve with initial calibration verification (ICV) check. The ICV must be within the 90-110% acceptance range.

11.9 Use continuing calibration verification (CCV) standards (which must be within the 90-110% acceptance range) at the beginning and end of every 10 samples to verify the calibration curve.

12. PROCEDURE:

12.1 Digestion:

12.1.1 To a 20 mL sample, add 5 mL of digestion solution.

12.1.2 Add 3 to 5 Teflon boiling stones. Too many boiling stones will cause the sample to boil over.

12.1.3 Set the Westco Block digestor at 160°C. Place tubes with samples in digestor and heat for one hour at 160°C. After one hour heat the samples at 380°C for two and a half hours.

12.1.4 Cool the sample and dilute to 20 mL with ammonia free water.

12.2 Automated Colorimetric procedure set-up on auto-analyzer 3 high resolution.

12.2.1 Ensure the 660 nm filters are in the colorimeter for TKN.ANL method.

12.2.2 Place all feed lines into de-ionized water containing Brij-35 and switch on all Auto-analyzer 3 modules. The valve for the column must be in the closed position.

12.2.3 To start the pump, close the pump platen. Set the power switch located on the side of the pump to position 1, which is on. Set the red switch on top of the pump to position RUN and the black switch to position normal. The rollers will now start rotating.

12.2.4 Check bubble pattern in all lines, especially the flow cell waste line.

12.2.5 Check the Water baseline by starting charting option in AACE to display charts with the channel readings. The water baseline should be stable and flat before continuing.

12.2.6 Place the reagent lines from the wash receptacle into the reagent containers. Check that the bubble pattern is still okay with reagents and that the baseline is stable and flat.

12.2.7 Select set-up and select analysis. In analysis select TKN.ANL method. Select new run to enter the sample information. Select O.K. to save after all the samples have been entered. Name the sequence by the date started (year, month, day).

12.2.8 Load the standards and samples into the tubes according to sequence. Start the run and select the date of the run for the sequence and select O.K.

12.2.9 Follow the run-log sequence and print data reports when done.

13. CALCULATIONS:

13.1 Results are calculated with the AA3 6.04 software.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT:

14.1 Use Clinical Laboratory of San Bernardino, Inc. procedures for Waste Disposal.

15. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA:

15.1 If the calibration is good and the CCV, LCS, MBLK pass the minimum requirements, the batch QC passes and samples can be analyzed. Batch must be re-run if CCV, LCS, or MBLK do not pass QC requirements.

16. REFERENCES:

16.1 Seal Auto Analyzer 3 High Resolution, Method G-310-04 Rev. 1

16.2 Method 351.2, "Total Kjeldahl Nitrogen (Colorimetric, Semi-Automated Digester, AAII)." US Environmental Protection Agency. (1993).

17. TABLES, DIAGRAMS, FLOW CHARTS, Etc:

17.1 Standard Preparation Table

Standard Name	Initial Conc. (mg/L)	Amt. Added (mL)	Final Conc.(mg/L)	Final Volume (mL)
Cal-1	1000	0	0	500
Cal-2	1000	0.5	1	500
Cal-3	1000	2.5	5	500
Cal-4	1000	5	10	500
Cal-5	1000	12.5	25	500
Cal-6	1000	20	40	500
Cal-7	1000	25	50	500
DLR*	1000	0.5	1	500
LCS*	1000	12.5	25	500
MS*	1000	0.5	25	20
ICV/CCV	1000	12.5	25	500

*Uses a secondary source standard (SDS) for preparation.

18. TRAINING AND QUALIFICATION VERIFICATION:

18.1 Signature of analyst and trainer on file with data.

19. HEALTH AND SAFETY:

19.1 Use of protective eyewear, rubber gloves and lab coat are required when running this method.

Department: Inorganics

Method Approved By:

Khurshid Ahmed
Department Supervisor

Date: _____

Bob Glaubig
Laboratory Director

Date: _____

Alex Popa
QA/QC Manager

Date: _____