

U4R07

CHARACTERIZATION OF NITROGEN GREENHOUSE GAS EMISSIONS FROM WASTEWATER TREATMENT BNR OPERATIONS

FIELD PROTOCOL WITH QUALITY ASSURANCE PLAN

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1 PROJECT DESCRIPTION AND OBJECTIVES

1.1 Problem Definition/Background

The push to achieve greater nitrogen removal from wastewater treatment plants, while minimizing infrastructure investments and operating costs, has resulted in the development of a wide range of innovative biological nitrogen removal (BNR) processes. However, BNR strategies could be a significant contributor to atmospheric NH_3 and NO depending upon the reactor configurations and operating conditions. In the future, as BNR is implemented at wastewater treatment plants around the nation, the flux of these gases to the atmosphere could significantly increase. Such increased releases would be a major concern since the greenhouse impact of nitrous oxide is about three hundred times that of carbon dioxide. Furthermore, nitric oxide is converted to nitrogen dioxide in the atmosphere, which is a precursor to photochemical smog (ozone).

1.2 Project Description

The goal of this WERF project is to characterize nitrogenous emissions from the activated sludge portion (only) of wastewater treatment plants. This project represents one of the first attempts at characterizing nitrogenous GHG emissions from wastewater treatment plants, and developing a methodology for collection of full scale plant data from a range of nutrient removal facilities in the United States. Building on previous work by the project team, this information will be integrated into an activated sludge model 1 (ASM 1) based mechanistic process model, which will be refined through this project through the addition of autotrophic pathways for NH_3 and NO emission. The refined mechanistic model will allow the industry to codify the results of this research, and develop a tool that will aid in the prediction and therefore mitigation of NH_3 , NO and N_2O emissions from WWTPs utilizing a range of wastewater treatment processes. Ultimately, this could allow the wastewater sector to engineer strategies for wastewater treatment that minimize gaseous nitrogen oxide emissions.

1.3 Project Objectives

According to the guidance on Quality Assurance project planning provided by USEPA National Risk Management Research Laboratory (NRMRL), projects can be divided into 4 categories:

- Category 1 is a study intended to generate data for enforcement activities,
- Category 2 is a study to generate data in support of the development of environmental regulations.
- Category 3 is an applied research project to demonstrate the performance of accepted processes under defined conditions.
- Category 4 is a study to generate data to evaluate unproven theories or to develop potential processes.

This research project is a Category 3 study. The objectives of this project will be to:

1. Identify principal aqueous and gaseous intermediates in activated sludge tanks under different configurations, nitrogen loads, and operating conditions (i.e. extant dissolved oxygen concentrations)
2. Determine the relative mechanisms and contributions of oxidative and reductive pathways in gaseous nitrogen oxide production by activated sludge bacteria
3. Develop a tool based on ASM algorithms augmented to allow the results of this research to be codified and available for use. The tool will facilitate optimization of nutrient removal processes to minimize both aqueous and gaseous nitrogen GHG emissions.

These project objectives will be accomplished in part by direct data collection during three inter-related components: bench-scale reactors experiments conducted entirely by Columbia University under the direction of Dr. Kartik Chandran, Principal Investigator; characterization of nitrogen greenhouse gas emissions from full scale wastewater treatment operations (nitrification/denitrification process tanks) also under the direction of Dr. Chandran; and collection of conventional wastewater parameters in conjunction with the full-scale gas emissions monitoring by participating wastewater treatment facilities under collaboration with Dr. Chandran. All of the participating wastewater treatment facilities have laboratory capabilities that are in compliance with their respective plant permits.

2 PROJECT ORGANIZATION

2.1 QA Management

WERF is a leader in research for the Clean Water sector (wastewater and stormwater utilities regulated under the Clean Water Act). WERF research also includes our volunteer advisory committees (Project Steering Committee), a group of highly-qualified subscriber practitioners, academics, and technology leaders, who provide oversight and technical direction to each research program to complement the WERF Program Director and the research teams. WERF actively abides by the applicable regulations established by USEPA at 40 CFR Parts 30 and 31, as well as all applicable reporting, auditing, and financial management requirements. WERF will utilize its existing organizational management structure, systems, and processes already in place to support timely implementation of quality assurance (QA). WERF has instituted a quality management system in conformance with ANSI/E4 standards, and has adopted a highly-effective Quality Management Plan, which is reviewed and updated regularly.

2.2 Documentation and Records

A printed copy (MS Word®) of the most recently updated version of the QAPP will be present in the offices of the principal investigator, the Program Director and QA Project Officer. A printed master copy of the current QAPP will be maintained in a dedicated binder in the Environmental Biotechnology Laboratory, Columbia University (Mudd Building, Room 1041) for ready reference to laboratory personnel. In addition, the binder will contain hard copies of routinely generated calibration curves, audit reports, detailed standard operating procedures for each analytical method or instrument used in the project and copies of chain of custody forms.

A printed copy (MS Word®) of the most recently updated version of the QAPP will also be provided to the contact person identified at each participating and TCR facility. Detailed records of sampling and analytical procedures and the measured results will be maintained in the laboratory notebooks of the respective laboratory personnel. Laboratory notebooks at Columbia University will be maintained per Kanare, 1985 (2). Difficulties encountered during sampling and analysis will be documented in the laboratory notebooks. Documented sampling and analysis problems will be discussed and resolved during weekly meetings held at Columbia University under the supervision of Dr. Chandran and during monthly PSC conference calls.

Problems during sampling and analysis may also be resolved by contacting the Project QA Officer, if necessary. Additionally, the manufacturer of the monitoring and laboratory equipment being used may be contacted directly.

2.3 Responsibilities of Project Participants

The organization of responsibilities to ensure efficient functioning of various tasks associated with the project is per Figure (1). Dr. Kartik Chandran will serve as Principal Investigator and overall Project Manager. The research team will consist of Prof. Krishna Pagilla from the Illinois Institute of Technology, Dr. Dimitri Katehis from CH2M Hill, Dr. Sungpyo Kim, Research Scientist, Columbia University and Joon Ho Ahn, Doctoral Candidate Columbia University.

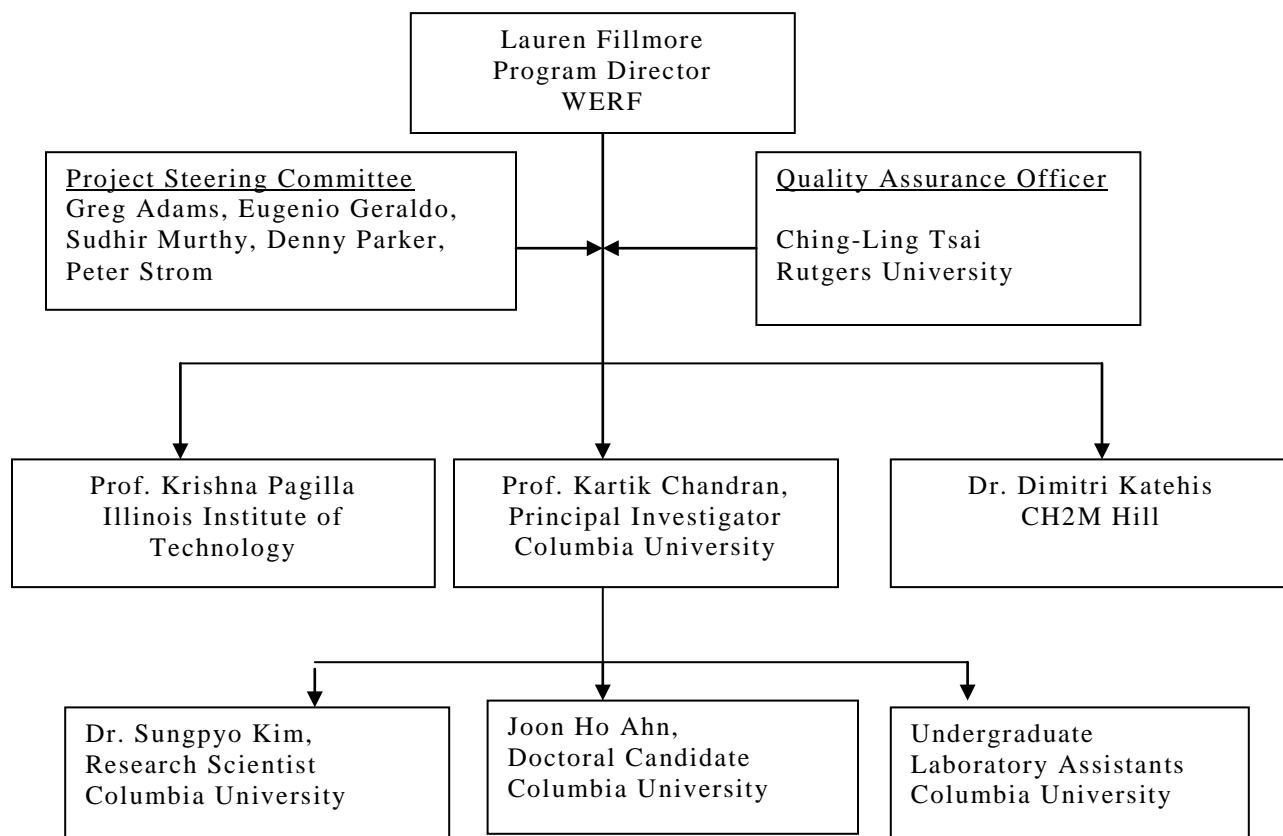


Figure 1. Project Organization Chart

2.4 Research Team Special Training Requirements/Certification

All laboratory personnel in the Columbia University Biomolecular Environmental Sciences (CUBES) Laboratories have undergone prior training on using different analytical instruments or methods. Additional training will be provided during new personnel initiation by respective equipment custodians. All field and laboratory personnel from Columbia University will undergo a mandatory Chemical and Biological Safety Training Course before routine monitoring commences and at least once every year, thereafter.

Each analytical instrument in the Environmental Biotechnology Laboratory at the Columbia University has a designated Custodian. The equipment custodians are expected to be fully cognizant of the standard operating procedures of their respective equipment. In addition, the custodians are responsible for training new users in the proper operation of the instrument. Operator competence will be checked (after operator training) by evaluating single operator precision on five replicate analyses of an independently prepared check sample. The concentration of the check sample will be from 5 to 50 times the method detection limit for a given analysis (3)

2.5 Project Schedule

The project is expected to follow the timeline below (Figure 2)

	Apr-Jun 2008	Jul-Sep 2008	Oct-Dec 2008	Jan-Mar 2009	Apr-Dec 2009
Objective 1a Full-scale monitoring – 5 WWTPs					
Objective 1b Full-scale monitoring - TCR					
Objective 2 Modeling					
Objective 3 Mechanisms of N emission					
Objective 4 Reporting and Outreach					
Deliverables and milestones	1. Event Sampling Data report.			60 days after each event	
	2. Draft WERF Report Final WERF Report			Spring 2009 Fall 2009	
	3. Calibrated ASM-N model published			Fall 2009	
	4. Workshop at WEFTEC 2009 on Sustainable Wastewater Treatment			Fall 2009	
	5. Session on Sustainable wastewater treatment at NYWEA 2010			Winter 2010	

Figure 2: Timeline for Specific Tasks

3 EXPERIMENTAL APPROACH

3.1 Sampling Design for Full-Scale Monitoring

The treatment trains of selected wastewater treatment plants that are accomplishing nitrification and denitrification will be characterized based on their liquid phase and gas-phase nitrogen concentrations and speciation. Testing will be conducted at each location during a sampling campaign during which gas phase monitoring will be conducted in real-time continuous mode and liquid phase sampling will be conducted via discrete grab sampling. Trends and variations in gaseous emissions and speciation will be ascertained. This sampling effort will assist in the development of process operating criteria that minimize both gaseous and liquid phase nitrogen emissions from wastewater treatment facilities. Sampling for nitrogen GHG compounds and precursors in both the air and liquid phases will be performed by Columbia University researchers. Conventional wastewater parameters will be sampled and analyzed by facility personnel corresponding to a preset regime in collaboration with the principal investigator.

Monitoring of the liquid-phase and the gas-phase will be conducted once in warm temperature conditions (i.e. summer, early fall), and cold temperature conditions (winter/early spring) in the Northeast and Midwest and twice in plants along the West Coast (Fall and Spring), not subject to significant temperature changes.

4 SAMPLING PROCEDURES – NITROGEN GHG EMISSIONS

Sample source: Treatment train from full scale wastewater treatment facilities

Location: Several BNR and non BNR plants

4.1 Sampling Design

The overall procedure for measuring CH_4 , NO and N_2O fluxes from the head-space of activated sludge tanks involves a variant of the EPA/600/8-86/008 and the South Coast Air Quality Management District (SCAQMD) tracer methods. This variant has been developed to measure those sources that have a relatively high surface flux rate when compared to diffusion which facilitates increased sampling at of composting and wastewater treatment plants across the country. A detailed description of the procedure is provided in Appendix A - Protocol.

Commercially available replicas of the US EPA surface emission isolation flux chamber (SEIFC) will be used to measure gaseous N fluxes from activated sludge reactors. The SEIFC consists of a floating enclosed space from which exhaust gas is collected in a real-time or discrete fashion. Since the surface area under the SEIFC can be measured, the specific flux of the gaseous compound of interest can be indirectly determined. The SEIFC ‘floats’ on the activated sludge tank surface and several replicate measurements

can be taken at different locations in a single tank as well as from different tanks (nitrification, denitrification) along a treatment train.

The SEIFC is also equipped with mixing (physical mixer or via sweep gas circulation) to ensure adequate gas and in some cases, an online temperature probe. The SEIFC is currently one of the few devices accepted by the USEPA for measuring gaseous fluxes (1) and as such will be employed for this study. Gas-phase analyses will be conducted via infra-red () and chemiluminescence (NO_x) methods. Detailed description of the analyzer equipment is provided in Appendix A- protocol.

In general, sampling will be conducted at multiple locations of the activated sludge train in each wastewater treatment facility. These locations the aerobic, anoxic and anaerobic zones, depending upon the configuration of the given facility.

Full-scale measurement of gas fluxes will be conducted at different locations along the activated sludge train at each full-scale wastewater treatment facility. Based on a fundamental understanding of the biological pathways that contribute to fluxes from activated sludge, the transition between the aerobic and anoxic zones is expected to be point contributing most to these fluxes.

Nevertheless, at each plant, , NO and emissions will be monitored from anoxic and aerobic zones. Typically, we anticipate sampling at one point in each anoxic zone and each aerobic zone with active nitrification along the treatment train.

During the course of the gas phase sampling, liquid phase samples will be collected adjacent to the hood location. The samples will be filtered immediately upon collection in the field and analyzed by host plant personnel for ammonia, nitrite and nitrate concentration, utilizing readily available field methods (i.e. a Hach Kit). As the primary purpose of these measurements is to ensure the presence of the targeted nitrogen species, without consideration to accuracy in the concentration measurements, the simplest available field method will be used for these preliminary measurements. Profiles of the nitrogen species along the aeration tank will be collected using the plants standard sampling and analysis procedures as outlined in Section 6.

4.2 Sampling Methods for Nitrogen GHG Emissions

4.2.1 Gas phase sampling method in Aerobic Zones

- i. Seal all but one vent in the flux chamber and connect high sensitivity pressure gauge to the one open vent.
- ii. Lower flux chamber into aerobic zone (bottom of rim should be below the surface of the water by 1-2 inches minimum).
- iii. Wait for analyzer to equilibrate based on stability indicator (<0.03)
- iv. Pull the flux chamber up. Open two vents and connect the analyzer, NO_x analyzer. The other vents should be left open to atmosphere.
- v. Record temperature of the gas in the flux chamber using a digital temperature gauge (Fisher Scientific number 15-077-8 or suitable alternate)

- vi. Care must be taken not to have the flow going to the two analyzers exceed the gas-flow rate from the flux-chamber. Otherwise, atmospheric air will be drawn in through the vents in the flux chamber.

4.2.2 Determination of gas flow rate from the flux chamber in Aerobic Zones

- vii. Disconnect CO_2 and NO_x analyzers and connect one outlet vent to the inlet line of a field gas chromatograph equipped with a thermal conductivity detector. Close the other vent.
- viii. Introduce tracer gas (10% He, 90% zero air) through an inlet vent into the flux chamber at a known flow rate (for instance 1L/min).
- ix. Measure the concentration of He gas exiting the flux chamber (protocol in appendix A).
- x. Based on the measured He concentrations, calculate via linear algebra the flow rate of aeration tank headspace gas entering the flux chamber (equation 1 provided in Appendix).

4.2.3 Gas phase sampling method in Anoxic Zones

- i. Seal all but one vent in the flux chamber and connect high sensitivity pressure gauge to the one open vent.
- ii. Lower flux chamber into anoxic zone with a (1-2 inch minimum submergence, into the liquid surface)
- iii. Wait for N_2O analyzer to equilibrate based on stability indicator (<0.03)
- iv. Pull the flux chamber up. Open two vents and connect the CO_2 analyzer, NO_x analyzer and the **sweep gas pump (Note: sweep gas only used during anoxic zone sampling)**. The other vents should be left open to atmosphere.
- v. Record temperature of the gas in the flux chamber using a digital temperature gauge (Fisher Scientific number 15-077-8 or suitable alternate).
- vi. Care must be taken never to have the flow going to the two analyzers exceed the sweep gas rate or dilution air will be drawn in through an opening in the chamber.

4.2.4 Determination of gas flow rate from the flux chamber in Anoxic Zones

- vii. Disconnect CO_2 and NO_x analyzers and connect one outlet vent to the inlet line of a field gas chromatograph equipped with a thermal conductivity detector. Close the other vent.
- viii. Introduce sweep gas to the chamber at a flow rate of 4L/min and wait 6 min for steady-state.
- ix. Introduce tracer gas (10% He, 90% zero air) through an inlet vent into the flux chamber at a known flow rate (for instance 1L/min).
- x. Measure the concentration of He gas exiting the flux chamber (protocol in appendix A).
- xi. Based on the measured He concentrations, calculate via linear algebra the flow rate of aeration tank headspace gas entering the flux chamber (equation 2 provided in Appendix).

Table 2 summarizes the data recording requirement checklist that needs to be followed for flux-chamber set up and operation. Additional analytes can be added by sampling teams based on a case specific basis. Details of liquid phase parameters and variables needed are presented in Tables B-1 and B-2.

Table 2: Checklist for Flux Chamber Set-up and Operation in Field

Measurement	Sampling Location 1	Sampling Location 2	Sampling Location 3
Gas flow rate from flux chamber			
Gas temperature in flux chamber			
Wastewater temperature			

4.3 Continuous and real-time Measurement

1. Turn on the power by pressing the on/off switch on the front panel. The display should turn on and green (sample) status LED should be energized. The green LED should blink indicating the instrument has entered the HOLD-OFF mode. Sample mode can be entered immediately by pressing the EXIT button on the front panel. The red "fault" light will also be on until the flows, temperatures and voltages are within operating limits. Clear the fault messages. After the warm-up, review the TEST function values in the front panel display by pushing the left most keyboard button labeled TEST.
2. Activate the instrument DAS data acquisition and set the sampling frequency for 1 sample per minute
3. Start data acquisition.
4. Connect the inlet tubing of the analyzer to the outlet tubing from the SEIFC securely using a standard 1/4" compression fitting connector.
5. Acquire data for about 20 min in anoxic zones and about 10 min in aerobic zones **after** stable readings are obtained- as indicated by the stability indicator on the analyzer.
6. Terminate the DAS software and immediately save the acquired data.
7. Repeat steps 2-5 for each sampling point and sampling locations (individual tanks).

Measurement range

0-1000 ppm

Calibration

At the beginning and end of each sampling event, the instrument will be calibrated using "zero gas" and standard gas as per manufacturer's instructions.

4.4 Continuous and Real-time NO and Measurement

1. Turn on the power by pressing the Power switch on the front panel and the external vacuum pump and wait till the display reads “MEAS” (this should typically take less than thirty minutes).
2. Activate the instrument data acquisition software and set the sampling and data save frequency for 1 sample per minute and 10 minutes, respectively. Start data acquisition.
3. Connect the inlet tubing of the analyzer to the outlet tubing from the SEIFC securely using a standard 1/4” compression fitting connector.
4. Acquire data for about 20 min in anoxic zones and about 10 min in aerobic zones **after** stable readings are obtained- as indicated by the stability indicator on the analyzer.
5. Terminate the CLD software and immediately save the acquired data.
6. Repeat steps 2-5 for each sampling point and sampling locations (individual tanks).

Measurement Range

Adjustable, 0-100 ppm

Calibration

At the beginning and at the end of each sampling day, the instrument will be calibrated using “zero gas” and NO standard gas as per manufacturer’s instructions

4.5 Measurement of Liquid-Phase Concentrations

In addition to measuring gaseous phase concentrations in the headspace of aerobic and anoxic zones, the liquid-phase concentrations will be measured to discriminate between generation in the liquid phase and emission in the gas phase. Liquid-phase concentrations will be measured using a polarographic Clark type electrode (Unisense, Aarhus, Denmark). For additional details of the liquid phase measurements summarized in this section, please refer to the Appendix.

1. Withdraw about 20 ml sample from test reactors in 50 ml conical centrifuge tubes or alternate similar containers (plastic or glass beakers are acceptable).
2. Take out the microsensor from the calibration chamber (containing deionized water), rinse out with deionized water, and mop dry with a tissue.
3. Immerse the microsensor into the samples. **Proceed as rapidly as possible after acquiring the sample.**
4. Record the numbers from the display on the picoammeter. The measurement numbers should be stable within one minute.
5. Pull out the microsensor, rinse out and place it back into the calibration chamber.
6. Repeat steps (1) ~ (5) for each sampling point and location.

4.6 Sample Collection Responsibilities

The measurement of nitrogen GHG emissions and collection of samples using the flux chamber will be done by Columbia University researchers and field technicians under the

direct supervision of Dr. Kartik Chandran. As the measurement of these parameters will be conducted by real-time analyzers or *in-situ* liquid probes, there is no need for sample handling and preservation. The real-time data from the analyzers or probes will be automatically downloaded on to a field computer or recorded in laboratory notebooks under the control of the Columbia University researchers. All electronic data will be backed up immediately upon return to New York to a duplicate location in the Environmental Biotechnology Laboratories at Columbia University . Additionally, where feasible electronic data will be stored on a temporary disk drive (in addition to the PC hard drive) during the field testing events.

5 SAMPLING PROCEDURES – WASTEWATER CHARACTERIZATION DATA

Sample source: Treatment train from full scale wastewater treatment facilities

Location: Several BNR and non BNR plants around the country

5.1 Sampling Design

Facilities that are selected to participate in an initial sampling effort will need to characterize influent flow, organics and nitrogen concentrations to the facility, in preparation for the detailed liquid and air measurement campaign. For the initial sampling the following parameters will be monitored from the secondary process, including the following as outlined in the Appendix (Table B-1):

- Influent Flowrates (minimum of once per hour)
- Influent and Effluent Ammonia (up to 8 times per day)
- Influent and Effluent Nitrite & Nitrate
- Influent and Effluent COD (assume once per hour, can be reduced depending on variability at site)

Additionally, diurnal performance and in-tank profiles according to Table B-2, in Appendix B, will be gathered at the time of the N GHG phase sampling. To the degree feasible, all liquid phase analyses will be according to approved methods and protocols that are used to gather data for regulatory NPDES or SPDES permits at the participating facilities. Where deviations from existing protocols are necessary, they will be documented in the Site Specific Sampling Plan (Appendix D). The Site Specific Sampling Plan will identify the site specific details related to sampling timelines and methods, analytical methods utilized, in addition to any deviations from the facility's standard operating protocols and procedures.

Note: To the extent possible, the sampling team will work with the laboratory personnel of the participating facilities to include data from online analyzers present at a given test site to avoid duplication of data gathering efforts.

5.2 Sampling Methods

Sampling will be conducted in accordance with the host WWTP's standard operating procedures, after review of said procedures by the project team. Sampling will involve use of autosamplers and manual sampling devices, as appropriate to support the sampling outlined in the protocol (Appendix B, Table B-1 and B-2).

5.3 Sample Collection Responsibilities

The collection of conventional wastewater samples for analysis of parameters in Table 3 will be conducted by facility personnel who usually collect operational and compliance samples for each participating facility. In advance of each sampling event, the Columbia University researchers will consult with laboratory personnel to ensure that samples for the conventional parameters are collected during the GHG monitoring event to meet the requirements of both the research design and the host facility's laboratory operating procedures.

5.4 Sample Handling and Custody Requirements

To the extent possible, the host utility's sample handling and custody requirements will be utilized for each field sampling campaign. To confirm adequacy of procedures, approximately two weeks prior to the full scale testing the host utility's procedures for field sample handling and chain of custody will be reviewed with the project team. At that time, if modifications are deemed necessary by the project team, they will be defined and documented in the Site Specific Sampling Protocol.

6 TESTING AND MEASUREMENT PROTOCOLS

6.1 Analytical Methods Requirements for Wastewater Characterization Data

Table 3 provides the sample location, the chemical parameter, sample container, preservative and holding time for samples to be collected during the operation of the bench scale reactors at the Columbia University Laboratory. For the full scale field testing, each host utility's laboratory will follow their specific laboratory standard operating procedures for each parameter. Standard Operating Procedures from participating laboratories will be included in the site specific protocol, a sample of which is included in Appendix C.

Table 3 : Sampling Specifications: Columbia University

Name of Chemical or Method	Measurement Classification		Sample Location	Sample Volume* (ml)	Sample Preservation	Maximum Holding Time
	Type	Frequency				
<u>Bench Scale Nitrifying Reactors</u>						
pH (Bench scale reactor)	C	NA	Bench scale reactor	Reactor	NA	None, online
Chemical Oxygen Demand – Colorimetric	I, C	2/7 d	35 ml glass vial	Reactor, Effluent	8	1 d
-N Potentiometric (ISE)	I, C	2/7 d	200 ml glass bottle	Effluent	80	Ψ 1 d
-N Spectrophotometric	I, C	2/7 d	200 ml glass bottle	Effluent	40	Ψ 2 d
-N Potentiometric (ISE)	I, C	2/7 d	200 ml glass bottle	Effluent	40	, pH < 2 28 d
Dissolved oxygen (Extant Respirometry)	C	4 Hz	100 ml respirometric vessel	Reactor	200	NA NA
	C	1/7 d	Gas sampling assembly**	Reactor headspace	NA	NA NA
NOx	C	1/7 d	Gas sampling assembly**	Reactor headspace	NA	NA NA
Dissolved oxygen (Bench scale Reactor)	C	NA	Bench scale reactor	Reactor	NA	NA None, online

*: The tabulated sample volume is twice that required for routine duplicate analysis and is apportioned into two sample containers. The additional volume is collected to determine quality control measures such as accuracy (analysis of spiked samples), precision (duplicate analysis) and to account for potential sample loss while handling or analysis. (Also see section 1.6)

C : continuous measurement I : intermittent measurement

Frequency of measurement applies only to continuous measurements

Ψ : Storage at . However, the biomass is removed from the sample via centrifugation at 3500 g for 10 minutes. Biomass removal arrests further biochemical oxidation of +N and -N. NA : Not applicable **: See protocol

6.2 Standardization of overall N-GHG Measurement Methodology

The overall procedure for measuring , NO and fluxes from the head-space of activated sludge tanks involves a variant of the EPA/600/8-86/008 and the SCAQMD tracer methods. Gas-phase analyses will be conducted via infra-red (N₂O) and chemiluminescence (NO_x) analyzers.

In the absence of an approved (USEPA or ASTM) method for N₂O in air or water, method modification was necessary to meet project objectives and measure N₂O emissions. To evaluate the performance of the measurement of , NO and fluxes using the procedure developed by the researchers, three side-by-side monitoring events were conducted along with the research procedure during the first sampling event at a step feed BNR facility. In addition to the research protocol performed by Columbia University staff, two additional side-by-side monitoring events were conducted as follows:

- Plant wastewater research engineers measured fluxes using the EPA isolation flux chamber and SCAQMD tracer method (confirm)but with a photo acoustic analyzer to directly determine N₂O.
- Chuck Schmidt, Ph.D. used the textbook EPA isolation flux chamber and SCAQMD tracer dilution method to measure the flux and the following analytical methods to measure ozone precursors and GHGs.

Table 5. Summary of Analytical Methodology by C. Schmidt

Method/Species	Technique	Application
ASTM Method 1946- Permanent Gas Analysis	GC/TCD	Relevant Fixed Gases: CH ₄ , CO, CO ₂ , and Helium as a separate analysis
NIOSH 6600	FTIR	N ₂ O, NO, NO ₂

These side-by-side tests using the NIOSH 6600 method were not designed to validate the modified analytical approach to establish an approved methodology; however, they provided an independent verification that the approach followed as part of this WERF project accurately measured N GHG emissions to meet the objectives of this research, for zones where concurrent side-by-side measurement was conducted.

Based on this side-by-side comparison, it was further recommended that the WERF project should consider the He tracer method (based on ASTM D1946) to measure gas flow rate from the flux chamber. This recommendation has since been incorporated in this protocol

7 QUALITY CONTROL REQUIREMENTS AND CORRECTIVE MEASURES

7.1 Quality Control (QC) of Laboratory Samples

Note: Established QC procedures already in place at field test facilities will supersede the QC procedures outlined in this QAPP.

Approximately 20% of the samples will be designated as QC samples: Recovery of known additions: 5%; split samples: 5% (bench-scale testing only); samples for duplicate analysis: 10%. The acceptance criteria for different QC measures are listed in Table 5. Note that known spikes are not feasible in the field for gas phase measurements due to transport limitation of hazardous gas cylinders.

Table 6: Quality Control Indicators of Analytical Data

Quality Control Indicator	Sample Type	Frequency	Parameter	Acceptance criterion (%)
Precision	Check standard	1 per 10	RPD	± 25
	Field Duplicate	1 per 10	RPD	± 25
	Lab Duplicate	1 per 10	RPD	± 25
Accuracy	Known spike	1 per 20	% recovery	75 – 125
Completeness	All	Annual	% missing	To be determined
Performance audit	Known sample	≥4/Year	RPD	± 10

RPD : Relative Percent Deviation (see Eqn. 4 below)

Data Quality Objectives (DQOs) will be expressed in terms of the following data quality indicators. The developed DQOs will be used to accept or reject data obtained during this study.

7.1.1 Precision

Precision is a measure of the closeness with which multiple analyses of a given sample agree with each other. Precision will be expressed as relative percent difference (RPD) of duplicate measurements (and).

$$RPD = \frac{(X_1 - X_2) * 100}{((X_1 + X_2) / 2)} \quad (4)$$

Instrument or method precision will be determined by duplicate analysis of stable standards. Overall precision of the study will be determined from duplicate samples subjected to identical sampling, sample preparation and analyses. Overall precision measures will reflect random errors in sampling, and variations in sample preparation and analysis. The precision of both field and lab duplicates will be measured (5).

7.1.2 Accuracy

Accuracy reflects the degree of confidence in a measurement. The accuracy of measurement techniques and analytical instruments will be checked by examining the percent recovery of sample spikes of a known composition. The percent recovery is defined as :

$$\% \text{ recovery} = \left(\frac{C_s - C}{s} \right) \times 100 \quad (5)$$

where :

- : spiked sample concentration
- C : sample background concentration
- s = concentration equivalent of analyte added to sample

Note : The total concentration after the sample spike should be within the linear calibration range of the method. Further, the volume change due to the spike should be negligible (3)

7.1.3 Representativeness

Representativeness is the extent to which measurements actually depict the true environmental condition or population being evaluated. For lab-scale reactors operated with constant influent loading, grab samples will be collected to ensure spatial (aerobic or anoxic zone, settling chamber) and temporal (consistent time and day of sampling during the week for a continuous flow reactor or consistent point along a sequencing batch reactor cycle) representativeness. This metric applies only to the lab-scale reactor element of the study.

7.1.4 Completeness

Completeness is a measure of the number of samples needed to provide useful information describing the system under investigation, compared to the total number of samples collected. Initially, for bench-scale reactors, all samples will be collected in 100% excess to permit quality control analysis or re-analysis owing to sample loss or data not complying with set DQOs. For instance, four samples will be collected, although only duplicate analysis will be performed routinely. Quality control analysis will be performed on 20% of the total samples routinely analyzed.

Completeness will be expressed as the percentage of the total number of measurements that are judged valid according to data quality objectives standards.

7.1.5 Comparability

Comparability is the extent to which data from one study can be compared directly to past data. The influent dynamics of aqueous and gaseous nitrogen species from the lab-scale reactors will be compared to those from similar operating conditions based on past records maintained in the lab.

7.1.6 Recovery of Known Additions

The accuracy of an analysis will be assessed by measuring the recovery of a sample spiked with a known concentration of a given analyte. 10% of the total samples collected will be used for the recovery of known additions. The analyte spike concentration will be between 5 and 50 times the MDL or between 1 and 10 times of the ambient concentration, whichever is higher (3). Again, this analysis is restricted to liquid-phase samples.

7.1.7 Analysis of Externally Supplied Standards

Externally supplied standards will be analyzed whenever analysis of known additions does not result in acceptable 25% recovery or once every day, whichever is more frequent (3). The concentrations of the standards will be between 5 and 50 times the MDL or near ambient sample levels (3). External standards will either be certified laboratory control standards or laboratory standards prepared independently from calibration standards (3).

7.1.8 Calibration with Standards

The electrical response of all analytical instruments will be linearly correlated to at least three analyte concentrations before each analysis. Typically, laboratory measurements that are within the linear calibration range will be reported. If the entire calibration range is not covered during a certain measurement, concentrations above the highest standard will be reported only if the following conditions are satisfied (3):

- Past evidence from earlier calibration curves obtained at identical instrument settings

- Measured value is less than 1.5 times the highest calibration standard.

On the lower end, the lowest reported value will be the MDL, provided that the lowest calibration standard is less than 10 times the MDL. If a method requires the response of blanks to be subtracted from the response of test samples, negative results will be reported as such or as below the limit of detection (3).

7.1.9 Analysis of Duplicates

10% of the total samples or one per analytical batch (whichever is more frequent) will be analyzed in duplicate. Using duplicate measurements, the precision of analytical technique (lab duplicate) or precision for the entire project (field duplicate) will be evaluated.

7.2 Performance Audits

7.2.1 Monitoring Lab Analysis (Bench-scale Testing)

Performance audits to monitor lab performance will entail analysis of unknown samples (analytes in Table 1) obtained from a lab supply company (e.g., Fisher Scientific Co., NJ). Performance audit samples will be analyzed at Columbia University before analysis of actual samples. Prior analysis of performance audit samples will ensure that the laboratory is well equipped in terms of (a) instruments, (b) standard operating procedures and (c) competent personnel for the continuous monitoring operation. A list of the audit activities and results will be present in the office of the principal investigator. If analysis of performance audit samples is not satisfactory (measured average outside $\pm 10\%$ of the actual audit sample value), errant data between two consecutive audits may be discarded and re-sampling or re-analysis may be warranted.

7.2.2 Monitoring Standard Operating Procedures

One unscheduled performance audit will be performed by the QA project officer. The audits will be conducted using a checklist made to document the protocol followed by the sampling crew and analysts while sampling, sample handling and storage, analysis, reporting of results (Table 6). Any deviations from the standard operating procedures maintained will be recorded in the laboratory notebooks of sampling personnel and corrective action will be taken to minimize future discrepancies. Further, in such case, the results obtained via non-standard protocols will be reviewed. If necessary, the results will be discarded and the stored samples will be re-analyzed as appropriate and if available. If the modification in the standard operating procedure improves the existing method, changes will be incorporated in the standard procedures.

Table 7: Sample Performance Audit for Sampling Nitrifying Bench-Scale Reactors

Standard Procedure	Performed	Remarks
Sample point from well mixed region (below aeration tube)	Yes	Tube cleaned thoroughly before introducing into reactor
Sample labeled and particulars entered in logbook	Yes	Date and time of sample Sampling personnel Sample volume Analyte to measure : $^+$ -N, $^-$ -N, tCOD
Sample split evenly	No	Sample not well mixed during split
Sample acidified	Yes	Conc. , (2ml/L)
Sample storage	Yes	, 28d holding time

7.3 Corrective Measures

Unsatisfactory data (not meeting DQO specifications, see criteria in Table 6) could result from flaws in the instrument or poor analyst skills. In case of unsatisfactory data quality, corrective measures will include a thorough troubleshooting of analytical instruments as recommended by the manufacturer and re-calibration of instruments using fresh reagents and standards. Further, the Standard Operating Procedure performance audits will also be checked to ensure competence of analysts and to conduct re-training, if necessary. In any case, deviant data will be discarded and re-sampling or re-analysis of stored samples will be performed.

7.4 Instrument Calibration, Maintenance and Quality Control Checks

Equipment used in continuous reactor operation such as pumps (Cole-Parmer, IL), DO controllers (Cole-Parmer, IL) or pH controllers (Cole-Parmer, IL) will be checked daily as part of routine reactor maintenance. In case of malfunction, the instrument will be disconnected from the reactor and re-calibrated, or replaced. The reactors will be temporarily shut down only if necessary. Currently, we have an extra set of reactor accessories in our laboratory for emergency repair measures.

The filling solution of the HNU ammonia gas sensing electrode will be changed once every three weeks, and the electrode membrane cap will be changed once every three months (HNU systems, MA). When not in use for short periods, the electrode will be stored in a 140 mg/l $^+$ -N solution. The manufacturer of the $^-$ -N ISE (Hach Co., CO) recommends that the electrode membrane tip should be

changed whenever a low slope of the calibration is observed (< 55 mV/decade). During continuous use, the electrode will be stored in a 100 mg NH_4^+ -N/L solution without ionic strength adjustor (ISA) added.

For NH_4^+ -N and NO_3^- -N measurement using potentiometric methods and NH_4^+ -N measurement using the phenate method, a fresh calibration curve (at least three points, e.g., 10, 100, 1000 mg/l, encompassing the concentrations to be measured) will be constructed for every analytical batch. From past experience and current analysis, the variability in calibration curves for colorimetric COD and NO_3^- -N measurement is small and therefore these calibration curves will be updated once every month. The individual points of the calibration curve will be generated from duplicate measurements. Calibration standards will be purchased from commercial vendors (e.g., from HACH Co. for COD standards) or prepared according to Standard Methods (e.g., for NH_4^+ -N, NO_3^- -N and NO_2^- -N) (3). All calibration curves will be stored on a personal computer to compare time-dependent variation in instrument characteristics or degradation of standards. After analysis of ten samples, a single-point calibration will be performed (preferably at the mid point of the multi-point calibration). If the single-point continuing calibration deviates by more than 25% from that of the multi-point curve, the analytical run will be terminated. A new multi-point calibration will be performed and all samples analyzed after the last satisfactory single-point calibration curve will be re-analyzed. Weighing devices such as balances or scales will be checked with class S weights once every month.

For continuous reactor operation, the feed pumps will be calibrated manually once every week. The pH and DO meters used for continuous monitoring and control will be respectively calibrated by using standard pH solution or saturated DI water at reactor operating temperature ($^{\circ}\text{C}$) once every month. All pipettes will be calibrated according to manufacturers' instructions once every six months.

The O_2 and NO_x analyzers will be calibrated at least once every six months (as per manufacturers' instructions and past measure of their stability) and before and after each sampling campaign using zero gas and CO_2 (500 ppm) and NO (10 ppm) gas standards.

7.5 Inspection/Acceptance Requirements for Supplies and Consumables

All reagents used in reactor operation and chemical or biological assays will be of highest purity necessary (typically ACS grade). Appropriate tubing and hoses will be used for specific applications (e.g., nontoxic Pharmed[®] tubing will be used to supply feed solution to reactors, Masterflex[®] corrosion-resistant tubing will be used for intermittent acid or base addition to reactors for pH control). Reactor tubing will be routinely checked visually for microbial growth and cleaned using DI water, once every two weeks or more frequently, if necessary. Fresh tubing will be installed every two months. Newly purchased supplies (e.g., Sample containers) will be washed using standard methods (3) before use. Evaluation of possible

measurement artifacts due to sampling or storage equipment will be part of QC analysis (Section 7.1).

8 DATA REPORTING, DATA REDUCTION AND DATA VALIDATION

Periodic data generated during the course of this study will be compiled weekly by the individual personnel conducting the respective experiments and analyses. The compiled data will be presented during weekly progress meetings held under the supervision of Dr. Chandran at Columbia University and monthly PSC conference calls.

8.1 Data Verification

The process of data verification determines whether data has been collected in accordance with specifications outlined in the QAPP. The four criteria for data verification are compliance, correctness, consistency and completeness.

Compliance: Compliance of data acquired during this project will be evaluated in terms of adherence to SOPs and satisfying QC criteria outlined in the QAPP (Table 6). Examples of data compliance evaluation tasks include:

Data Compliance Evaluation Task	Performed by
Staff Training and Certification	Project Manager
Sample Custodian Assignment	Project Manager
Field Data Collection Audit	Project QA Officer
Calibration of Instruments	Sampling Personnel
Confirming Verification of Calibration	Sampling Team Leader
Calibration Corrective Action Audit	Sampling Team Leader and Project QA Officer
Sample Preservation and Handling	Sampling Personnel

Correctness: Correctness of acquired data will be determined by checking if data analysis calculations were performed in accordance with properly documented and properly applied algorithms. Examples of data correctness evaluation tasks include:

Data Correctness Evaluation Task	Performed by
Instrument Inspection and Maintenance Audit	Sampling Team Leader
Instrument Calibration Review	Sampling Team Leader
Data Recording Audit	Project QA Officer
Data Reduction Audit	Project QA Officer
Data Transformation Audit	Project QA Officer
Raw Data Audit	Sampling Team Leader

Consistency: Consistency refers to the extent to which data collection and data reporting procedures were done in a reproducible manner. Consistency ensures that reported values of any given parameter or state variable are identical, when used at different times or locations in the Project. Examples of data consistency evaluation tasks include:

Data Consistency Evaluation Task	Performed by
Data Handling Audit	Project QA Officer
Data Transmittal Review	Project QA Officer

Completeness: Completeness is the extent to which all data necessary to perform validation analysis were actually collected. Completeness is based on DQOs outlined in the QAPP. Examples of data completeness evaluation tasks include:

Data Completeness Evaluation Task	Performed by
Documentation of Sampling Corrective Action	Sampling Team Leader, Sampling Personnel
Sample Records Documentation and Audit	Sampling Personnel
Sample Transport Documentation and Audit	Sampling Team Leader

Data Management audit	Project QA Officer
Chain of Custody Documentation	Sample Custodian
Sample Identification Audit	Project QA Officer
Instrument Inspection and Maintenance Documentation	Sampling Personnel
Traceability of Standards Review	Sampling Team Leader
Documentation of Calibration Corrective Action	Sampling Personnel

The results of data verification will be presented to the Project Manager by the Project QA Officer.

8.2 Data Validation for Bench-Scale Testing

Data validation is an evaluation of the technical usability of the verified data with respect to the planned objectives of the project. Data validation is performed following data verification. Data validation consists of the following:

1. Determine and ensure that data provide necessary information to make decisions or address project objectives
2. Assign qualifiers to individual data values. The assigned qualifiers indicate the degree to which the data can be used when drawing conclusions based on the entire data set. Examples of data qualification may include :
 - Analyte not detected above MDL
 - Concentration of analyte is approximate due to interference
 - Identification of analyte is uncertain due to interference
 - Concentration of analyte is confirmed
3. Assess applicability of certain performance criteria (e.g., DQOs) used to make decisions on measured data, based on data gathered during the course of the Project. For instance, information on the magnitude of analytical error for a certain method may result in re-evaluation of precision criteria.
4. Determine whether DQOs were satisfied and whether data can proceed to Quality Assessment (Data Quality Assessment consists of reviewing DOQs and sampling design, preliminary data review, selecting statistical tests, verifying assumptions and hypotheses and drawing conclusions).

Data validation will be conducted by the Project QA Officer. In addition, all data gathered will be reviewed by Project QA Officer every quarter. If the data

quality indicators do not meet the criteria outlined in the QAPP, data may be discarded or flagged with data qualifiers. Bench-scale test re-sampling or re-analysis may be conducted. If failure to meet DQOs is due to equipment failure, then calibration and maintenance of analytical instruments will be made more stringent. If failure to meet DQOs is due to inadequate expertise of sampling and analysis personnel, then they will be retrained in bench-scale testing methods.

8.3 Reconciliation with User Requirements

The principal investigators and the QA Officer will make decisions to either reject or qualify data based on criteria outlined in the Data Quality Objectives. (Also, see Corrective measures). Modifications may be warranted at various levels based on obtained results. Potential problems with data quality and any modifications to initial DQOs will be transmitted to the WERF Program Director via routinely held project conference calls.

Note on Data Verification and Validation: Based on results of data verification and validation, sampling and analysis may be repeated before achieving data that can successfully proceed to data assessment. If exhaustive corrective measures do not improve data quality, such data may not be used. However, if the requirements set forth in the QAPP are followed, most acquired data may be consistent with Project requirements and data rejection may be minimal.

9 ASSESSMENT AND OVERSIGHT

9.1 Assessments

Weekly meetings will be conducted at Columbia University to oversee the progress of the study, involving Prof. Kartik Chandran, Dr. Sungpyo Kim and Mr. Joon Ho Ahn. Monthly meetings involving the Project Managers, teams and the PSC will be conducted via conference calls to ensure efficient coordination between the activities at the sites around the country.

9.2 Reports to Management

The results of continuous monitoring of the full-scale reactors will be compiled within sixty days after a sampling event. Bench-scale monitoring reports will be submitted once a year following a review during the routine meetings held between the project team and the PSC.

9.3 Documentation and Records – Columbia University

A printed copy (MS Word®) of the most recently updated version of the QAPP will be present in the offices of the principal investigators. A printed master copy of the current QAPP will be maintained in a dedicated Binder in the

Environmental Biotechnology Laboratory, Columbia University (Mudd Building, Room 1041) for ready reference to laboratory personnel. In addition, the Binder will contain hard copies of routinely generated calibration curves, audit reports, detailed standard operating procedures for each analytical method or instrument used in the Project and copies of Chain of Custody forms. Detailed records of sampling and analytical procedures and the measured results will be maintained in the laboratory notebooks of the respective laboratory personnel. Laboratories notebooks will be maintained per Kanare, 1985 (2). Difficulties encountered during sampling and analysis will be documented in the laboratory notebooks. Documented sampling and analysis problems will be discussed and resolved during monthly PSC conference calls. Problems during sampling and analysis may also be resolved by contacting the Project Quality Officer, if necessary. Additionally, the manufacturer of the equipment being used may be contacted directly.

9.4 Documentation and Records – Participating and TCR WWTP Facilities

Each participating or TCR facility will receive a printed copy (MS Word[®]) of the most recently updated version of the QAPP which they will retain in the offices of the principal contact during the period of performance of this study.

Each laboratory conducting the analysis of wastewater samples for conventional parameters will follow their Standard Operating Procedures for records retention. Given the significant implications of the data generated from this study in the development of gaseous nitrogen emission factors from the wastewater treatment industry, the data sets will be stored for as long as feasible in both hardcopy and electronic format. Each participating WWTP facility will turn over the wastewater characterization data to the Columbia University research team, including QC results collected during each sampling event.

10 REFERENCES

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APPENDIX A - 1

PROTOCOL FOR MEASURING THE SURFACE FLUX OF NITROUS OXIDE (N₂O) AND NITRIC OXIDE (NO) FROM ACTIVATED SLUDGE TANKS

Prepared by: K. Chandran
Last edit: K. Chandran July , 2008
Filename: GaseousNProtocol.doc

INTRODUCTION

The following protocol, which has been prepared as part of this project, is intended to provide utilities and field sampling teams with a detailed description of the data collection methodology and analysis requirements to enable calculation of gaseous nitrogen fluxes from different zones of activated sludge trains in a wastewater treatment facility.

EQUIPMENT, MATERIALS and SUPPLIES NEEDED

1. Surface emission isolation flux chamber (commercially available from vendors, for instance, [://www.fivesenses.com/Prod_Emission.cfm](http://www.fivesenses.com/Prod_Emission.cfm) or custom built based on specifications from the United States Environmental Protection Agency (6).
2. Teledyne API Monitor Model 320E (Teledyne API, San Diego, CA)
3. EcoPhysics NO_x Analyzer Model CLD64 (EcoPhysics, Ann Arbor, MI)
4. Zero gas (containing zero ppm and NO), and and NO gas standards (Tech Air, White Plains, NY)
5. Dwyer series 475 Mark III digital manometers to measure flux chamber pressure from 0 to 1" (high sensitivity) and 0 to 100" (low sensitivity) of water column (Dwyer Instruments Inc., Michigan City, IN)
6. Rotameter to measure influent sweep gas flow rate, 0 - 30 L/min, (Fisher Scientific, Fairlawn, NJ)
7. Adjustable air pump, 0-10 L/min (Fisher Scientific, Fairlawn, NJ) to provide sweep gas flow into the flux chamber
8. Vacuum pump, 0-30 L/min (Fisher Scientific, Fairlawn, NJ) for active pumping of gas from the flux-chamber (never required based on sampling campaigns conducted to date)
9. 0.2 µm cartridge filters, set of 10 (Millipore, Ann Arbor, MI) to prevent fine particulates from entering the gas analyzers
10. Silica Gel column for capturing moisture (Fisher Scientific, Fairlawn, NJ)
11. Glass water trap consisting of a 100 ml glass bottle placed in ice within a Styrofoam[®] box
12. Teflon[®] tubing (approximately 0.5") and fittings
13. 100-300' extension cord and power strip
14. Laptop personal computer (with at least 512 MB RAM) with data acquisition programs for and NO_x analyzers pre-installed
15. Set of miscellaneous hand-tools including adjustable wrenches, different size screw drivers and adjustable pliers.

EXPERIMENTAL PROCEDURE

The overall procedure for measuring NH_3 , NO and N_2O fluxes from the head-space of activated sludge tanks involves a variant of the EPA/600/8-86/008 and the SCAQMD tracer methods, which allow sampling of gaseous emissions from high surface flux rate operations.

Commercially available replicas of the United States Environmental Protection Agency surface emission isolation flux chamber (SEIFC) will be used to measure gaseous N fluxes from activated sludge reactors. The USEPA SEIFC essentially consists of a floating enclosed space through which, carrier gas (typically nitrogen or argon) is fed at a fixed flow rate and exhaust gas is collected in a real-time or discrete fashion. Since the surface area under the SEIFC can be calculated or measured, the specific flux of the gaseous compound of interest can thus be determined. Since the SEIFC ‘floats’ on the activated sludge tank surface, several replicate measurements can be taken at different locations in a single tank as well as from different tanks (nitrification, denitrification) along a treatment train. The SEIFC is also equipped with mixing (physical mixer or via sweep gas circulation) to ensure adequate gas and in some cases, an online temperature probe. The SEIFC is currently one of the few devices accepted by the USEPA for measuring gaseous fluxes (I) and as such will be employed for this study.

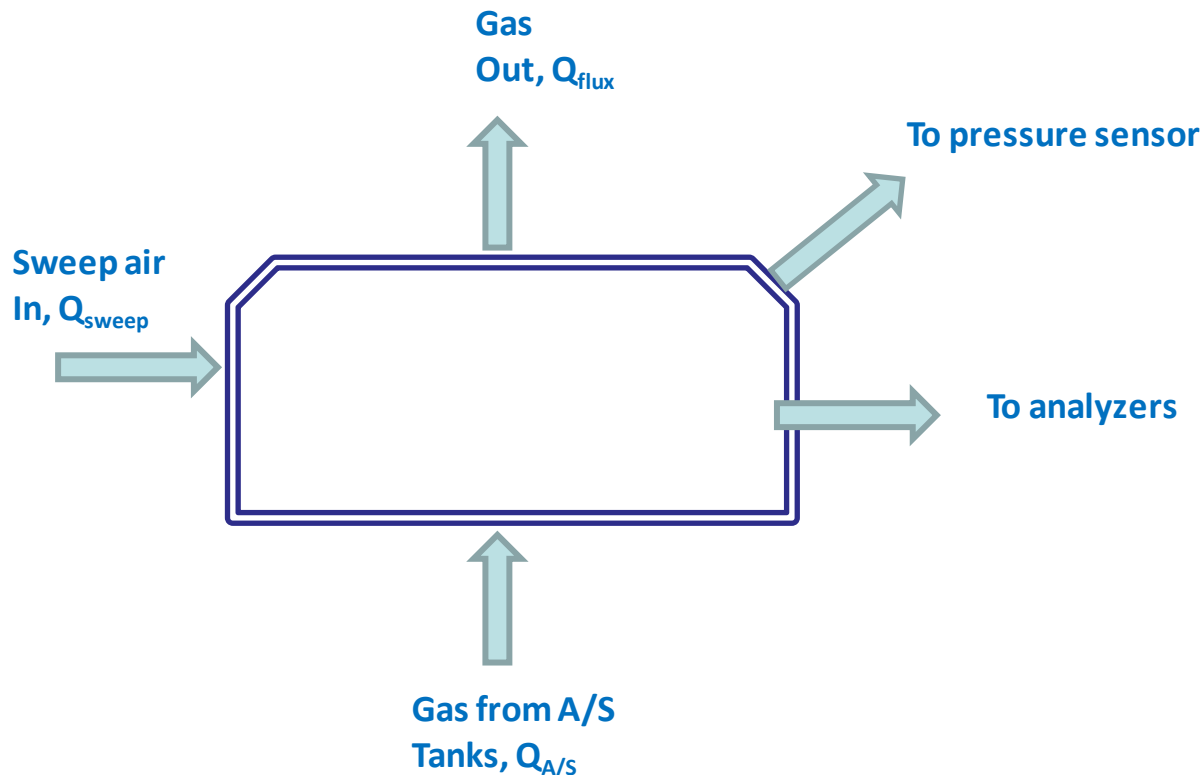


Figure A1: Full-scale measurement of nitrogen gases will be done using the USEPA surface emission isolation flux chamber (modified from (1))

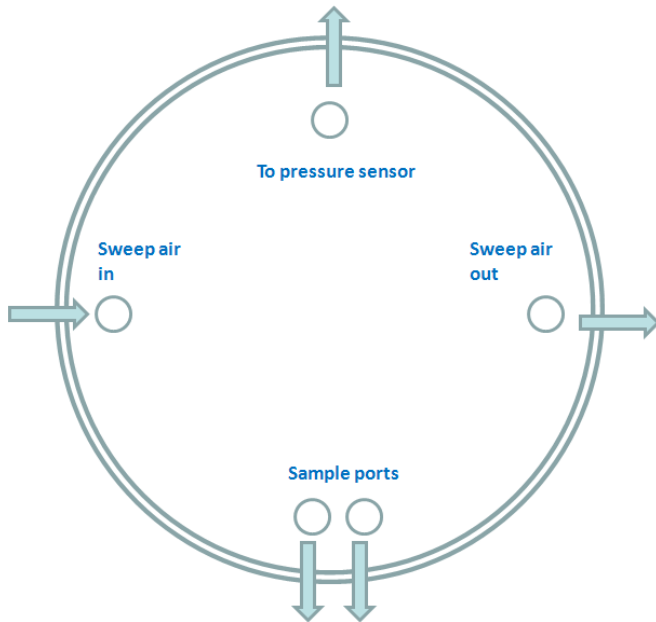


Figure A2: Modified schematic of the flux chamber

In general, sampling will be conducted at multiple locations of the activated sludge train in each wastewater treatment facility. These locations the aerobic, anoxic and anaerobic zones, depending upon the configuration of the given facility. Additionally, within each zone, multiple points (approximately three, but not less than two) will be sampled to address any variability in gas fluxes that may result due to variations in mixing or flow patterns therein.

Pressure build up can be minimized by equipping the flux chamber with multiple vents or a variable size vent and continuously monitoring the pressure drop across the hood using a

sensitive pressure gauge. In this study, the latter approach (pressure gauge) will be followed to monitor the pressure across the flux chamber. In all field locations, gas flow rate will be measured using the tracer gas technique and pressure will be passively monitored if necessary. Alternately, the aeration rate from plant records (available as a order of magnitude verification) have also been used to estimate VOC fluxes from aeration tanks and a similar approach could be used in this study (Dr. Chuck Schmidt, personal communication). The modified set up of the flux chamber used in this study is depicted in Figures A1-A3.

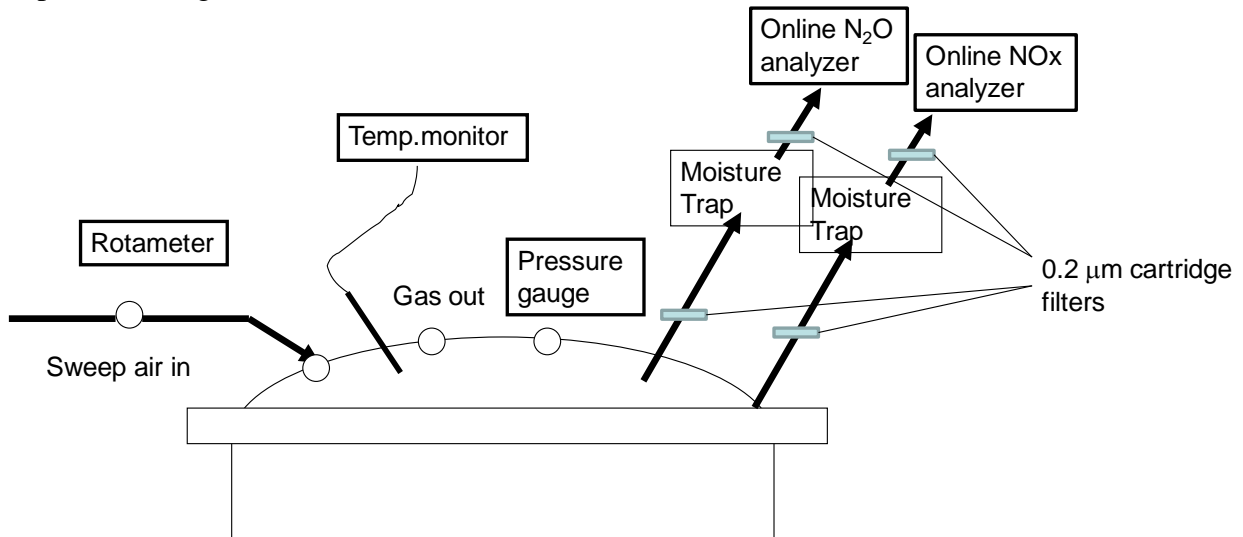


Figure A3: Schematic of flux-chamber set-up for N₂ and NO_x flux measurements

Gas phase sampling method in Aerobic Zones

1. Seal all but one vent in the flux chamber and connect high sensitivity pressure gauge to the one open vent.
2. Lower flux chamber into aerobic zone (bottom of rim should be below the surface of the water by 1-2 inches minimum).
3. Wait for analyzer to equilibrate based on stability indicator (<0.03)
4. Pull the flux chamber up. Open two vents and connect the analyzer, NOx analyzer. The other vents should be left open to atmosphere.
5. Record temperature of the gas in the flux chamber using a digital temperature gauge (Fisher Scientific number 15-077-8 or suitable alternate)
6. Care must be taken not to have the flow going to the two analyzers exceed the gas-flow rate from the flux-chamber. Otherwise, atmospheric air will be drawn in through the vents in the flux chamber.

Gas phase sampling method in Anoxic Zones

1. Seal all but one vent in the flux chamber and connect high sensitivity pressure gauge to the one open vent.
2. Lower flux chamber into anoxic zone with a (1-2 inch minimum submergence, into the liquid surface)
3. Wait for N₂O analyzer to equilibrate based on stability indicator (<0.03)
4. Pull the flux chamber up. Open two vents and connect the analyzer, NOx analyzer and the **sweep gas pump (Note: sweep gas only used during anoxic zone sampling)**. The other vents should be left open to atmosphere.
5. Record temperature of the gas in the flux chamber using a digital temperature gauge (Fisher Scientific number 15-077-8 or suitable alternate).
6. Care must be taken never to have the flow going to the two analyzers exceed the sweep gas rate or dilution air will be drawn in through an opening in the chamber.

Figure A-4 summarizes the data recording requirement checklist that needs to be followed for flux-chamber set up and operation. Additional analytes can be added by sampling teams based on a case specific basis. Details of liquid phase parameters and variables needed are presented in Tables A-1 and A-2.

Measurement	Sampling Location 1	Sampling Location 2	Sampling Location 3
Pressure in flux chamber			
Gas flow rate from flux chamber			
Gas temperature in flux chamber			
Wastewater temperature			
Air-pump flow rates			

Figure A-4: Checklist for flux-chamber set-up and operation in field

Continuous and real-time measurement

Measurement

1. Turn on the power by pressing the on/off switch on the front panel. The display should turn on and green (sample) status LED should be energized. The green LED should blink indicating the instrument has entered the HOLD-OFF mode. Sample mode can be entered immediately by pressing the EXIT button on the front panel. The red "fault" light will also be on until the flows, temperatures and voltages are within operating limits. Clear the fault messages. After the warm-up, review the TEST function values in the front panel display by pushing the left most keyboard button labeled TEST.
2. Activate the DAS data acquisition software and set the sampling frequency for 1 sample per minute.
3. Start data acquisition.
4. Connect the inlet tubing of the analyzer to the outlet tubing from the SEIFC securely using a standard 1/4" compression fitting connector.
5. Acquire data for about 20 min in anoxic zones and about 10 min in aerobic zones **after** stable readings are obtained- as indicated by the stability indicator on the analyzer.
6. Terminate the DAS software and immediately save the acquired data.
7. Repeat steps 2-5 for each sampling point and sampling locations (individual tanks).

Measurement range

0-1000 ppm

Calibration

Before each sampling event, the instrument will be calibrated using "zero gas" and standard gas as per manufacturer's instructions

Continuous and real-time NO and measurement Measurement

1. Turn on the power by pressing the Power switch on the front panel and the external vacuum pump and wait till the display reads “MEAS” (this should typically take less than thirty minutes).
2. Activate the CLD data acquisition software and set the sampling and data save frequency for 1 sample per minute and 10 minutes, respectively. Start data acquisition.
3. Connect the inlet tubing of the analyzer to the outlet tubing from the SEIFC securely using a standard 1/4” compression fitting connector.
4. Acquire data for about 20 min in anoxic zones and about 10 min in aerobic zones **after** stable readings are obtained- as indicated by the stability indicator on the analyzer.
5. Terminate the CLD software and immediately save the acquired data.
6. Repeat steps 2-5 for each sampling point and sampling locations (individual tanks).

Measurement Range

Adjustable, 0-100 ppm

Calibration

Before each sampling event, the instrument will be calibrated using “zero gas” and NO standard gas as per manufacturer’s instructions

Principles of real-time , NO and measurements

Principles of measurement

Continuous measurements will be performed via infra-red (IR) gas-filter correlation, which is based on the absorption of IR radiation by molecules at wavelengths near 4.5 μm . As part of the measurement process, a broad wavelength IR beam is generated inside the instrument and passed through a rotating Gas Filter Wheel, which causes the beam to alternately pass through a gas cell filled with Nitrogen, (Measure Cell) and a cell filled with / Mixture (Reference Cell) at a frequency of 30cycles/sec. concentrations are inferred based on the amount of IR absorption at wavelengths close of 4.5 μm .

Ultimately, the ‘stripped’ beam strikes the detector which is a thermoelectrically cooled solid-state photo-conductor. This detector, along with its pre-amplifier converts the light signal into a modulated voltage signal.

Principles of NO and measurement

The chemiluminescence approach is based on the gas-phase reaction of NO with excess ozone (O_3), which produces a characteristic near-infrared luminescence (broad-band radiation from 500 to 3,000 nm, with a maximum intensity at approximately 1,100 nm) with an intensity that is proportional to the concentration of NO. **It should be noted that this is the same reaction via which NO causes the depletion of the ozone layer.**

Reaction chemistry involved in measurement of NO concentrations

1. $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ Formation of stable and excited by reaction of NO with

2. $* \rightarrow + h\nu$ Conversion of excited to stable with release of luminescent radiation

Reaction chemistry involved in measurement of concentrations

3. + reducing agent \rightarrow NO + oxidized reducing agent Reduction of to NO
4. NO measurement by chemiluminescence (Reactions 1 and 2)

To determine the concentration of NO by chemiluminescence, the sample gas flow from the nitrifying reactors is mixed with in a reaction chamber operated under negative pressure (vacuum). The chemiluminescence that results from these reactions is monitored by an optically filtered high sensitivity photomultiplier, that responds to chemiluminescence emission at wavelengths longer than 600 nm. The electronic signal produced in the photomultiplier is proportional to the NO concentration in the sample gas. Measurement of is achieved by means of a heated converter that reduces to NO.

APPENDIX A – 2 PROTOCOL FOR MEASURING LIQUID-PHASE NITROUS OXIDE

Prepared by: J-H. Ahn
Last edit: K. Chandran November , 2008
Filename: Liquid Phase Protocol.doc

EQUIPMENT NEEDED

1. Nitrous Oxide Microsensor N2O25 (Unisense, Aarhus, Denmark)
2. 2 Channel picoammeter PA2000 (Unisense, Aarhus, Denmark)
3. Calibration Chamber CAL300 (Unisense, Aarhus, Denmark)
4. Zero air and gas standard (Tech Air, White Plains, NY)
5. Teflon[®] tubing, Silicone tubing and fittings
6. Squeezer with deionized water
7. Kimwipes
8. BD Falcon 50 ml conical tubes

EXPERIMENTAL PROCEDURE

Principles

The Unisense nitrous oxide microsensor is a miniaturized Clark-type sensor with an internal reference and a guard cathode. In addition, the sensor is equipped with an oxygen front guard, which prevents oxygen from interfering with the nitrous oxide measurements. The sensor is connected to a high-sensitivity picoammeter and the cathode is polarized against the internal reference. Driven by the external partial pressure, nitrous oxide from the environment will penetrate through the sensor tip membranes and be reduced at the metal cathode surface. The picoammeter converts the resulting reduction current to a signal. The internal guard cathode is also polarized and scavenges oxygen in the electrolyte, thus minimizing zero-current and pre-polarization time.

Measurement steps

1. Turn on the power switch located on the front panel of picoammeter.
2. Check the 'Gain' screw for channel 1 is turned fully counter-clockwise.
3. Turn the display switch, located on the center of the panel, to 'Signal 1' and check that the display reads zero. If not, adjust the offset, as per the manufacturer's instructions.
4. Turn the display switch to 'Pol. 1'. Check if the polarization voltage shows -0.8 V. If not, adjust volt and polarity switch.
5. Connect the "pre-polarized" microsensor leads to the meter in the following order: (1) Signal wire (black) to 'Input' of channel 1 on the front panel. (2) Guard wire (yellow) to 'Guard' of channel 1.
6. Rinse out the sensor with deionized water and absorb the moisture with kimwipes.
7. Place the sensor into the calibration chamber which contains deionized water.
8. Select the 'Normal' setting for the 'Mode' switch on the front panel, unless you need the extremely fast response.

9. Select the appropriate measuring range using the 'Range' switch on the panel. Usually 200 pA is selected, but if not suitable, select an alternate range available.
10. Withdraw about 20 ml sample from test reactors in 50 ml conical centrifuge tubes or alternate similar containers (plastic or glass beakers are acceptable).
11. Take out the microsensor from the calibration chamber (containing deionized water), rinse out with deionized water, and mop dry with a tissue.
- 12. Immerse the microsensor into the samples. For (x) and (xii), proceed rapidly as possible after acquiring the sample.**
13. Record the numbers from the display on the picoammeter. The measurement numbers should be stable within one minute.
14. Pull out the microsensor, rinse out and place it back into the calibration chamber.
15. Repeat (10) ~ (14) for each sampling point and location.
16. When the measurements are complete, disconnect the sensor leads in the reverse order to which they were connected.

Measurement range

Adjustable, 0- 0.616 ppmv- (with 500 ppm gas standard)

Pre-polarization steps

If the sensor is new or has not been operated for several days, then it must be polarized for at least 2 hours and up to 12 hours before it can be calibrated and/or used.

1. Secure the nitrous oxide sensor with its tip, immersed in nitrous oxide free water.
2. Turn the display switch to 'Pol.1' and adjust the polarization to -1.30 V.
3. Turn the display switch to 'Signal 1' and adjust the 'Gain' screw completely counter-clockwise. Adjust the display to zero on the 'Offset' dial, if needed.
4. Connect the signal wire (black) of the microsensor to 'Input' terminal.
5. After 5 minutes, adjust the polarization to -0.8 V and then connect the guard wire (yellow) to 'Guard' terminal.
6. Pre-polarize for as possible up to 12 hours to get the maximum stability.

Calibration

After the sensor has been polarized, it must be calibrated with zero air and gas standards. Typically, we have used 500 ppm gas standards for calibration.

Note 1: gas standards are specialty items and can be purchased from vendors such as TechAir.

Note 2: To be consistent in terms of units for liquid and gas phase, the results of this study are expressed in terms of . Alternately, liquid and gas phase concentrations can also be expressed as "N" to estimate the fraction of influent nitrogen discharged as .

APPENDIX A – 3

**PROTOCOL FOR MEASURING EMISSION GAS FLOWRATE USING
HELIUM TRACER GAS METHOD (after ASTM Method D1946)**

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Reviewed by: D. Katehis, M. Ward, K. Chandran

Last edit: K. Chandran January , 2009

Filename: He Tracer Protocol.doc

In aerated or aerobic zones

1. Activate the field gas-chromatograph approximately prior to the actual helium (He) measurements to allow for the thermal conductivity detector (TCD) and GC column to attain the desired temperatures.
2. After measuring gas-phase and NO_x, disconnect the and NO_x analyzers and connect one outlet vent to the inlet line of the field GC. Close the other vent.
3. Introduce tracer gas (10% He, 90% zero air) through an inlet vent into the flux chamber at a known flow rate (for instance 1L/min).
4. Measure the concentration of He gas exiting the flux chamber (as per ASTM method D1946).
5. Based on the measured He concentrations, calculate via linear algebra the flow rate of aeration tank headspace gas entering the flux chamber (equation 1).

$$Q_{tracer} * C_{helium-tracer} = (Q_{tracer} + Q_{emission}) * C_{helium-GC}$$
$$Q_{emission} = \frac{Q_{tracer} * (C_{helium-tracer} - C_{helium-GC})}{C_{helium-GC}} \quad (1)$$

6. For each sampling location, conduct steps 2-5 at least three times

In un-aerated or anoxic zones

7. The only modification to the protocol for adaptation to measuring the emission flow rate from anoxic zones is the introduction of sweep gas.
8. Introduce sweep gas to the chamber at a flow rate of 4L/min and wait 6 min for steady-state.
9. Follow steps 2-6 as described above for determination of emission flow rate from aerobic zones.
10. Calculate the emission flow rate from the anoxic zone using equation 2

$$Q_{tracer} * C_{helium-tracer} = (Q_{tracer} + Q_{sweep} + Q_{emission}) * C_{helium-GC}$$
$$Q_{emission} = \frac{Q_{tracer} * (C_{helium-tracer} - C_{helium-GC})}{C_{helium-GC}} - Q_{sweep} \quad (2)$$

Note: Each sampling campaign consists of discrete and continuous measurements. During the discrete measurements, will be determined at each location in the treatment plant where is measured. During continuous measurements, will be determined several times a day in correspondence with liquid-phase measurements.

APPENDIX B

DATA ANALYSIS AND PROCESSING

Liquid-phase sampling in aerobic and anoxic zones

Preliminary Data Gathering and Steady State Process Analysis. The integral dependence of NH_3 and NO emissions on the process operating conditions make the development of a steady state analysis crucial. The following background information will need to be collected from candidate evaluation sites:

Overall Plant Description. Obtain general treatment plant configuration, liquid and solids process flow diagrams, design criteria, major mechanical process equipment, etc from the plant's design reports and/or O&M manuals. In addition, gather the following secondary process operating data:

- Secondary Process Configuration, including: Zone Configuration, operating set points, basins in services, aeration system (equipment, controls, monitoring capabilities), typical range of aeration rates, mixers (types, location, HP)
- Plant Operating Data. Summary of a minimum of three months plant data applicable to the treatment process to allow for characterization of the process influent, target and actual operating setpoints for key operational parameters (DO, SRT), effluent concentrations. Table B-1 provides an outline of typical data requirements. Where applicable, modifications to Table B-1 will be made as part of the generation of the Site Specific Sampling Protocol, to reflect plant configuration and operating characteristics.

Analyze the data collected using conventional techniques such as development of solids and nitrogen balances as well as through the use of the secondary process model. For the sake of brevity, details of model based evaluation are not presented in their entirety, since we expect to largely follow the procedure described in (7).

Intensive On-Site Sampling and Analysis

For facilities that are selected to participate an initial diurnal sampling effort will be conducted to characterize influent flow, organics and nitrogen concentrations to the facility, in preparation for the detailed liquid and air measurement campaign. For the initial diurnal sampling conventional parameters will be monitored from the secondary process as detailed in Table B-2, including:

- Influent Flowrate (minimum of once per hour)
- Influent and Effluent Ammonia (8 times per day)
- Influent and Effluent Nitrite & Nitrate (8 times per day, may substitute $\text{NO}_2^- + \text{NO}_3^-$ with subset N measurement)
- Influent and Effluent COD (assume once per hour, can be reduced depending on site)

Additionally, the following diurnal performance and in-tank profiles will be gathered according to Table B-2.

Table B-1. Data Requirements for Plant Screening

Sample Location	Analyte												
	TSS	VSS	Total	Sol.	Total	Sol. COD 0.45u	ff COD	Temp		Sol. TKN 0.45u	NH3-N 0.45u	NO3-N	NO2-N
Primary Effluent	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk	1/wk		1/wk	1/wk	1/wk	1/wk	1/wk
Secondary Effluent	1/wk	1/wk	1/wk	1/wk	1/wk	1/	1/		1/wk	1/wk	1/wk	1/wk	1/wk
Reactor MLSS	1/wk	1/wk						1/wk					
RAS MLSS	1/wk												
WAS MLSS	1/												
Clarifier	Blanket TSS (use sludge judge- 1/day and average once per week)												
Flow split and flow rate	<p>Different measurements possible</p> <ul style="list-style-type: none"> • Approximate- set PE gate and allow natural hydraulics (no info on range) • Confirm flow split by doing mass balance and MLSS concentrations • Alternately: take a measurement of MLSS at each pass: • Use Royce meter to get each pass TSS every 2-3 hours to get running average 												
Anoxic Zone Mixing	Mechanical or aerator driven												
Operating Data													
Influent Flow	Diurnal Flow Pattern at Appropriate Time Intervals (15 minutes for periods of rapid diurnal increase, 1 hour for stable periods)												
RAS Flow	Average weekly RAS Flow, Indicate location and type of flow measurement and variability of flow												
WAS Flow	Average weekly WAS Flow, Indicate location and type of flow measurement, times of WAS wasting if not continuous												
Dissolved Oxygen	1/day (then average weekly), indicate location of DO measurement along basin length and time of measurement												
Aeration Rate	Daily average, indicate location of Air Flow Measurement and variability over the course of the day. SCADA output at short time intervals would be best												
Pickle Liquor Consumption	Daily, indicate Ferric Chloride equivalent strength, dosing points and dose at each point												

¹ Homogenize subsample prior to “total” measurement. Discard remaining sample – **DO NOT** use for “filtrate” or “soluble” determinations

²: soluble COD can be used instead of ffCOD on the secondary effluent

³: when RAS and WAS are from the same stream, TSS measurement on one of these streams is sufficient

Table B-2. Data Requirements for Model Calibration

Sample Location	Analyte													
	TSS	VSS	Total	Soluble	Total	Sol. COD	ff COD		Sol. TKN	pH	Alk	NH3-N	NO3-N	NO2-N
Primary Effluent	8/d	2/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d
Secondary Effluent	8/d	-	8/d	8/d	8/d	8/	8/	8/d	8/d	8/d	8/d	8/d	8/d	8/d
RAS MLSS	8/d													
WAS MLSS	8/													
Operating Data														
Influent Flow	Diurnal Flow Pattern at Appropriate Time Intervals (15 minutes for periods of rapid diurnal increase, 1 hour for stable periods)													
RAS Flow	Average Daily RAS Flow, Indicate location and type of flow measurement and variability of flow													
WAS Flow	Average Daily WAS Flow, Indicate location and type of flow measurement, times of WAS wasting if not continuous													
Dissolved Oxygen	1/hr, indicate location of DO measurement along basin length and time of measurement													
Aeration Rate	Daily average, indicate location of Air Flow Measurement and variability over the course of the day. SCADA output at short time intervals would be best													
In-tank Profiles	TSS	VSS	pH	DO	ORP	Temp.	ff COD	Alk.	NH3-N	NO3-N	NO2-N			
	8/d	2/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d	8/d

Determination of fluxes

Calculate the net flux of gaseous N species (mg/min-) based on the gas flow rate out of the flux chamber (, L/min), gas concentration (parts per million) and the cross-sectional area of the SEIFC () (Equation 3).

$$\text{Flux} = \frac{Q_{\text{emission}} * C}{A} \quad (3)$$

Correct the calculated flux reflect standard temperature () and pressure (1 atm.).

Determination of lumped emission factors

Lumped emission factors for each facility will be computed based on the measured flux from each zone in the facility normalized to the daily influent total Kjeldahl nitrogen (TKN) loading (mass/mass) according to equation 4.

$$\text{Emission - factor} = \frac{\sum_{i=1}^n \text{Flux}_i * \text{Area}_i - (\text{kg} - \text{N}_2\text{O} - \text{N})}{\text{Daily - inf luent - TKN - load} - (\text{kg} - \text{N})} \quad (4)$$

Where:

= emission flux calculated from the zone (kg -N/-d)

= Surface area of the zone ()

n = number of zones in a given facility from which fluxes are captured

It should be noted that the above calculations reflect the emission factor calculated from discrete measurements. In plants where significant diurnal variability exists, such variability will be accounted for by a combination of explicit measurements in select zones and mathematical modeling output of fluxes from remaining zones.

APPENDIX C

EXAMPLE OF SITE SPECIFIC SAMPLING PROTOCOL

The Site Specific Sampling Protocol (SSMP) will provide site specific sampling and analysis information. Care must be exercised to avoid duplication of the information present in the General Protocol, shown in Appendix A. The SSMP will provide sampling diagrams, sampling times and analytical methods used by the laboratory facilities. Modifications to the General Protocol will be outlined in the SSMP.

The Site Specific Sampling Protocol will consist of:

- Work Schedule: Provides times of initiation of sampling for each round for gas and liquid phase sampling
- Liquid and Gas Phase Sample Locations: Series of diagrams denoting approximate location of sampling locations
- Listing of Host Laboratory Analytical Methods
- Additional Documentation Requirements Deemed Necessary by the Project Team: This will include site specific log sheets, chain of custody forms, etc.
- Listing of Deviations from the General Protocol: Modifications to gas phase sampling equipment and liquid phase sampling approach. Modified tables B-1 and B-2 from Appendix B, where applicable would be included in this section.

The attached sample provides a template, however it is recognized that depending on the complexity and requirements of the sampling program at each location, the SSMP format may need to be modified.

Table C-1. Example Work Schedule

Work Schedule for N2O Testing

Date: 9/29/07

Sampling Round	Time	Location		Liquid Sampling Profile Start
		Flux Chamber No.1	Flux Chamber No. 2	
	0600 0800	Instrument Calibration Checks from Gas Standards. Placements of flux chambers for Round 1		X
Round 1	0900	Zone 1	Zone 6	
	0930			
	1000			
	1030			
Round 2	1100	Zone 2	Zone 5	X
	1130			
	1200			
	1230			
Round 3	1300	Zone 3	Zone 4	X
	1330			
	1400			
	1430			
Round 4	1500	Zone 7	Zone 12	
	1530			
	1600			
	1630			
Round 5	1700	Zone 8	Zone 11	X
	1730			
	1800			
	1830			
Round 6	1900	Zone 9	Zone 10	X
	1930			
	2000			
	2030			
	2100	Overnight Gas Phase Measurements at Selected Locations		

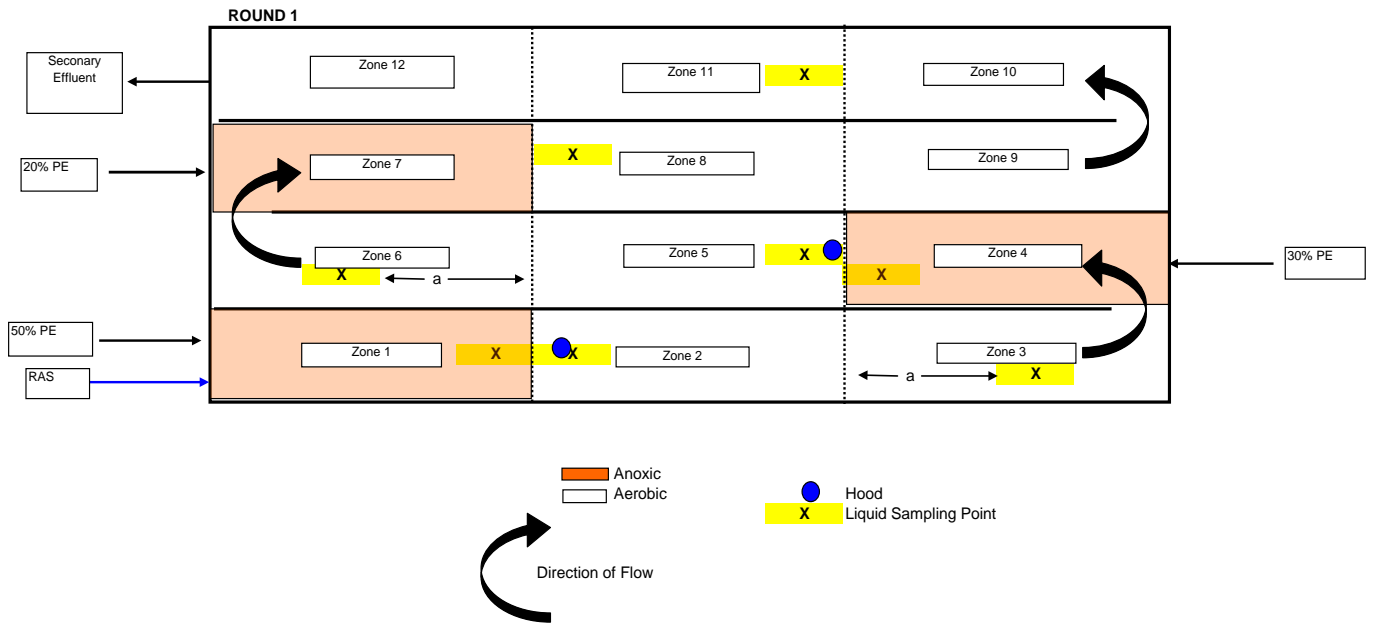


Figure C1. Ex. Sampling Location Diagram – Round 1(top) and Round 2 (bottom)

Table C-2: Listing of Host WWTP Analytical Methods (Sample)

Analyte	Method
TSS	SM Method 2540D
VSS	EPA Procedure 160.4 SM Method 2540E
cBOD	SM Method 5210B
COD (Total and Soluble)	SM Method 5220 C and D
ffCOD	SM Method 5220 C and D Mamais et al ¹
pH	SM Method 4500-H ⁺
TKN	SM Method 4500- Lachat Instruments QuikChem Method 10-107-06-2-D (EPA Method 351.2)
NH3-N	EPA Procedure 350.1 SM Method 4500-NH3-H Lachat Instruments QuikChem Method 10-107-06-1-I (EPA Method 350.1)
NO3-N	SM Method 4500- ⁻ -F Lachat Instruments QuikChem Method 10-107-04-1-A (EPA Method 353.2)
NO2-N	SM Method 4500- ⁻ -F Lachat Instruments QuikChem Method 10-107-05-1-A (EPA Method 353.2)
Nitrate-Nitrite	SM Method ⁻ F
Total Alkalinity	SM Method 2320B

- SM = Standard Methods for the Examination of Water and Wastewater, 18th Edition,
- EPA = Methods for the Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA-600/4-79-020, Revised March 1983,

¹ Mamais, D., Jenkins, D., and P. Pitt (1993), "A rapid physicochemical method for the determination of readily biodegradable soluble COD in municipal wastewater, Waster Research 27(1): 195-197.