

ABSTRACT

LARSEN, JULIE MELISSA. Measuring dinitrogen gas emissions from a lagoon treatment system. (Under the direction of John Classen, Sarah Liehr)

A method for collecting dinitrogen gas emissions from open pond waste treatment systems was developed. The method was critically tested in a laboratory for sources of air contamination to ensure reliable gas measurements. A laboratory experiment was done to estimate the rate at which dissolved dinitrogen would be stripped out of solution due to non-dinitrogen bubbles rising through the water column. A volumetric mass transfer coefficient for the process was estimated for clean water. The gas collection method was implemented in a partially aerated lagoon treatment system for dinitrogen and methane gas sampling. The volumetric mass transfer coefficient found in the laboratory for clean water was adjusted to compensate for field gas production rates, temperatures and wastewater quality to estimate the rate of stripped dinitrogen from the partially aerated lagoon. The estimated rate of stripped dinitrogen was subtracted from the total measured dinitrogen flux to estimate the dinitrogen produced biologically. Results from laboratory testing revealed that dinitrogen can be measured with low amounts of dinitrogen atmospheric contamination (0.57% N₂) and the preliminary field results suggest that biological denitrification did occur at this lagoon treatment system.

MEASURING DINITROGEN GAS EMISSIONS FROM A
LAGOON TREATMENT SYSTEM

By

JULIE MELISSA LARSEN

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master's of Science

BIOLOGICAL AND AGRICULTURAL ENGINEERING

Raleigh

2003

APPROVED BY:

Co-Chair of Advisory Committee

Co-Chair of Advisory Committee

BIOGRAPHY

In May of 2000, Julie Melissa Larsen received her Bachelor's Degree in Environmental Engineering from the Civil Engineering Department at North Carolina State University. This paper represents the final requirement for a M.S. in Biological Engineering at North Carolina State University. Julie will join Youth with a Mission (YWAM) Marine Reach in January 2004 and go through their 5-month discipleship training school. YWAM Marine Reach is a non-profit Christian ministry that provides free medical and engineering services to the poor coastal communities in the Pacific Ocean.

ACKNOWLEDGEMENTS

Many people have contributed to this research project and I would like to acknowledge and thank them for their support. My advisors Dr. Classen, Dr. Sarah Liehr and Dr. Wayne Robarge have helped me tremendously with the planning and direction of this project. Many thanks goes to Dr. Pedro Luna for his hard work and long hours collecting gas samples, liquid samples, and other field measurements. Bob Seila from the Environmental Protection Agency in Research Triangle Park, NC, kindly donated the SUMMA® canisters used in this research. Roberto Munilla and Brian Phillips from North Carolina State University also helped significantly in the design and building of the field implementation of the gas collection method. Laboratory analysis of liquid samples and gas samples was provided by Rachel Huie and Christine Hayes of the Biological Engineering Department at North Carolina State University. I would also like to thank the Battelle Memorial Institute for providing some of the funding for this research and the InStream™ Water Unit used in the lagoon treatment system. The most important acknowledgement goes to my Lord Jesus, my personal Friend and Savior.

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES	vi
LIST OF SYMBOLS	vii
1.0 INTRODUCTION	1
2.0 EXPERIMENTAL DESIGN AND METHODS.	5
2.1 Testing Gas Chromatography.	7
2.2 Testing Gas Collection Method.	8
2.3 Testing to Estimate a Volumetric Mass Transfer Coefficient.	11
2.3.1 Calculations	12
2.4 Field Implementation of Gas Collection Method	14
2.4.1 Calculations	19
3.0 RESULTS AND DISCUSSION.	22
3.1 Gas Chromatography.	22
3.2 Gas Collection Method Testing.	22
3.3 Estimation of Mass Transfer Coefficient.	23
3.4 Field Implementation of Gas Collection Method.	25
4.0 CONCLUSIONS.	29
REFERENCES	31
APPENDIX	
Appendix A – Part Numbers and Materials Tables.	35
Appendix B – Detailed Procedures.	40
Appendix C – Data tables.	47
Appendix D – Pictures.	50
Appendix E – Calculations	53
Appendix F – Drawings.	60

LIST OF TABLES

Table 1.	Testing gas chromatography method.....	22
Table 2.	Experiment 1: Results from testing gas collection method with initial low dissolved oxygen and dinitrogen concentrations for air contamination	23
Appendix		
Table A1.	Materials used to make the SUMMA® can devices used in this research	36
Table A2.	Materials used for the carboy device, not including the flotation device.	37
Table A3.	Materials used for flotation device.	37
Table A4.	Other material/equipment that are not shown in tables A1, A2, A3	38
Table A5.	Supply company information	39
Table C1.	Dinitrogen and methane emissions from the lagoon treatment system . .	48
Table C2.	Estimations of the stripped dinitrogen from field data and using an alpha value of 0.7	49
Table C3.	The estimated rate of stripping and biological emissions (using an alpha value of 0.7).	49

LIST OF FIGURES

Figure 1.	Summa Canister® with fittings and valves	7
Figure 2.	Diagram of experimental design for testing gas collection method	9
Figure 3.	Device used to implement gas collection method	16
Figure 4.	Diagram of lagoon treatment system with dimensions	17
Figure 5.	InStream™ Water Unit installed in the lagoon treatment system.....	18
Figure 6.	Picture showing InStream™ Water Unit, gas collection device, and two hanging baffles	18
Figure 7.	Dissolved oxygen measurements over time for diffused air and diffused helium in a tank filled with clean water	24
Figure 8.	Dinitrogen flux measurements and stripping estimations using an alpha of 0.7	25
Figure 9.	Relationship between estimated stripped N ₂ flux when using an alpha value of 0.7 with measured non-dinitrogen flux	27
Appendix		
Figure B1.	Diagram of aluminum bars and tabs used to build the flotation device	44
Figure B2.	Diagram to show the top view of flotation device and the nuts and bolts locations.....	46
Figure B3.	Diagram of styrofoam and fiberglass boards bolted together.....	46
Figure D1.	Disks inside the InStream™ Water Unit used in the lagoon treatment system.....	51
Figure D2.	Picture of the lagoon treatment system with InStream™ Water Unit and hog houses.....	51
Figure D3.	Picture of Dr. Luna taking sample from gas collector.....	52
Figure D4.	Pigs inside hog house.....	52
Figure E1.	Diagram for the two-film theory for gas transfer.....	55
Figure F1.	Drawing of carboy frame rotated to at an angle.....	61
Figure F2.	Drawing of carboy frame with dimensions and detailed bolt view.....	62

LIST OF SYMBOLS

a_{field}	= total specific area (At/V) in field conditions, $m^2 m^{-3}$; used in equation (9)
a_{lab}	= total specific area (At/V) in lab conditions, $m^2 m^{-3}$; used in equation (9)
At	= total bubble surface area, m^2 ; used for equation (9)
C	= the bulk solution concentration, $g m^{-3}$ used in equations (2), (3), (4), (5)
C_e	= equilibrium concentration $g m^{-3}$; used in equation (6)
C_i	= the initial bulk solution concentration, $g m^{-3}$; used in equation (4)
C_s	= the saturation concentration that is equilibrium with a gas phase; used in equation (4)
C_{s_atm}	= saturation concentration that is equilibrium with the gas phase in the atmosphere, ($g m^{-3}$); used in equation (2), (6)
C_{s_bubble}	= the saturation concentration at the surface of the bubble, assumed to be in equilibrium with the bulk gas phase, $g m^{-3}$; used in equations (3)
$[k_L a]_{bubble}$	= liquid volumetric mass transfer coefficient for transfer at the surface of the bubble, sec^{-1} ; used in equations (3), (4), (5), (6)
$[k_L a]_{cleanwater}$	= liquid volumetric mass transfer rate in clean water, sec^{-1} ; used in equation (8)
$[k_L a]_{field}$	= liquid volumetric mass transfer rate adjusted for field conditions, sec^{-1} ; used in equation (9)
$[k_L a]_{lab}$	= liquid volumetric mass transfer rate found in laboratory testing, sec^{-1} ; used in equation (9)
$[k_L a]_{process\ water}$	= liquid volumetric mass transfer rate in process waste water, sec^{-1} ; used in equation (8)
$[k_L a]_{surface}$	= liquid volumetric mass transfer coefficient for transfer at the surface of the tank, sec^{-1} ; used in equations (2), (4), (6)
$[k_L a]_{total}$	= liquid volumetric mass transfer coefficient including surface and bubble transfer, sec^{-1} ; used in equation (4)
$[k_L a]_T$	= liquid volumetric mass transfer coefficient at temperature, T °C, sec^{-1} ; used in equation (7)
t	= time, sec; used in equations (1), (2), (3), (4), (5)
T	= temperature, °C; used in equation (7)
Q_{field}	= gas production rate in a lagoon treatment system, $m^3 sec^{-1}$; used in equation (9)
Q_{lab}	= average gas flow rate used in experiment 2, $m^3 sec^{-1}$; used in equation (9)
V	= total liquid volume, m^3 ; used for equation (9)
Greek symbols	
α	= alpha factor defined in equation (8), dimensionless
θ	= theta factor defined in equation (7), dimensionless

1.0 INTRODUCTION

In many parts of the country, open pond treatment systems are favored methods for managing and treating animal waste, small municipality waste, and industrial waste because of the low capital cost and the minimal management required. One important goal of open pond treatment is nitrogen removal, which occurs as the result of a combination of ammonia volatilization, algal uptake, nitrification/denitrification, sludge deposition, and adsorption onto bottom sediment (Crites and Tchobanoglous, 1998).

The predominant mechanism for nitrogen losses from livestock waste management systems has been thought to be ammonia volatilization (Phillips, 1995). For example, Koelliker and Miner (1973) estimated an ammonia volatilization loss of $49 \text{ kg N ha}^{-1} \text{ d}^{-1}$ from an anaerobic swine lagoon based on the nitrogen lost in the mass balance calculations and not from direct measurement. Such estimates of ammonia volatilization from waste treatment systems have caused concerns because of ammonia's pungent odor that is noticeable at concentrations above 50 ppm (Phillips, 1995) and because of its suspected role in both air quality problems and nutrient enrichment due to deposition (Aneja et al., 2001; Walker et al., 2000).

However, all nitrogen loss from lagoon treatment systems may not be due to ammonia volatilization. Other mechanisms for nitrogen loss include N_2 production from the microbial processes of nitrification and denitrification. These mechanisms are preferred over ammonia volatilization because N_2 is harmless and inert. Many researchers doubt N_2 production is significant in anaerobic waste treatment lagoons because of the low dissolved oxygen concentrations. For nitrification, dissolved oxygen is necessary to oxidize ammonia to

nitrite and nitrate. In anoxic conditions, denitrification reduces nitrate and nitrite to N₂ gas. Typically, nitrification has been reported to occur in environments where the dissolved oxygen concentrations were higher than 1.0 mg L⁻¹ (Tchobanoglous and Burton, 1991). However, scientists have reported dinitrogen gas produced during anaerobic treatment of natural and synthetic waste (Poth, 1986; Bock et al., 1995; Mulder et al., 1995; van de Graaf et al., 1996; Schmidt and Bock, 1997; Harper and Sharpe, 1998; Jetten et al., 1999). Possible pathways for N₂ production include low oxygen nitrification (Bock et al., 1995), denitrification by nitrifying organisms (Goreau et al., 1980; Poth, 1986; Bock et al., 1995; Schmidt and Bock, 1997) and anaerobic ammonia oxidation (Mulder et al., 1995; Jetten et al., 1999). One study reported *Nitrosomonas eutropha* and *Nitrosomonas europaea* nitrifying with dissolved oxygen concentrations as low as 0.2 mg L⁻¹ (Bock et al., 1995).

Recent field studies of gas emissions from anaerobic swine lagoons by Harper and Sharpe (1998) provide evidence that dinitrogen gas is produced in amounts equal to or greater than ammonia. This study found ammonia emissions in the range of 4.9 to 10.5 kg NH₃ -N ha⁻¹ d⁻¹ and dinitrogen emissions ranging from 8.9 to 120 kg N₂-N ha⁻¹ d⁻¹. This level of N₂ production would require a source of oxygen to accomplish the initial ammonia-oxidizing step. The traditional term, “anaerobic” lagoon can be misleading because oxygen and dinitrogen diffuse into the lagoon at the atmosphere-lagoon interface. Jones et al. (2000) estimated a range of oxygen transfer rates at the air-water interface of an anaerobic lagoon with temperature of 20°C, dissolved salts at 5,000 ppm and wind speed ranges from 1 to 10 m/s to be 4.4 to 440 kg ha⁻¹d⁻¹. If all the molecular oxygen was used to convert ammonia to nitrite by ammonia-oxidizing microorganisms and the nitrite was used in denitrification,

these oxygen transfer rates are adequate to explain the measured N_2 flux by Harper and Sharpe (Jones et al., 2000).

Estimating denitrification from waste treatment systems by measuring N_2 gas emissions is difficult because of problems associated with sampling and stripping. Atmospheric contamination in gas sampling and analysis is a major concern because 78 % of dry air is composed of N_2 (Weiss, 1970). Another concern that may affect accurate estimations of denitrification is methane bubbles stripping dissolved dinitrogen as the bubbles rise through the water column. This may be significant in open treatment systems where the liquid is in equilibrium with the atmosphere. The saturation or equilibrium concentration of an atmospheric gas dissolved in water depends on the type of gas, its partial pressure in the atmosphere and the water temperature. Oxygen is about twice as soluble as dinitrogen, but the partial pressure of dinitrogen (78%) is almost four times the partial pressure of oxygen (21 %). This makes water in equilibrium with air almost twice as plentiful in dissolved nitrogen compared to dissolved oxygen (Harvey, 1975). Open pond treatment systems in equilibrium with the atmosphere may have extremely low dissolved oxygen concentrations due to biological activity; however, the concentrations of dissolved nitrogen should remain closer to saturation. Dissolved dinitrogen is biologically inert and the concentration will not be significantly affected by microbial activity like that of oxygen (McNeil et al., 1995). The concerns associated with air contamination and stripping have not been quantified with respect to measuring N_2 gas emissions from open pond treatment systems.

The goals of this research include designing a method for measuring dinitrogen gas emissions with minimal air contamination from a waste treatment system. The equipment and the method were critically tested in a laboratory to ensure reliable gas measurements and to quantify the amount of N₂ that could come from air contamination. A laboratory experiment was also used to estimate a dinitrogen volumetric mass transfer coefficient involved in the stripping process for clean water. The third objective of this study was to design and demonstrate a simple and safe implementation of the gas collection method and to use the method to quantify dinitrogen and methane emissions from an open pond treatment system. The amount of dinitrogen stripped from the open pond treatment system was estimated using an adjusted volumetric dinitrogen mass transfer coefficient that was determined from the laboratory experiment, compensating for different temperature, gas flow rate, and wastewater characteristics.

2.0 EXPERIMENTAL DESIGN AND METHODS

The gas collection method was modified from Harper and Sharpe's gas collection method (1998) and involves a submerged gas collector for trapping gas produced from an open pond treatment system and a storage device for transporting gas samples to a laboratory for N₂ gas analysis. The submerged gas collector was a 21-L Nalgene™ carboy (Clearboy, VWR International, Inc., Pittsburgh, PA) with the bottom cut off. A 3/8 in. diameter hole was cut in the center of the carboy lid and the following Swagelok® fittings (Raleigh Valve and Fitting, Raleigh, NC) were mounted on the lid: a stainless bulkhead reducer, plug valve and hose connector (see appendix A, table A2 for part numbers and appendix B, procedure B2 for detailed procedure). The fittings were securely sealed on the lid with a nut and two rubber washers. A contact adhesive and sealant called Outdoor Goop® was generously applied over each rubber washer and surrounding area. The carboy was marked in liter increments with black permanent marker. The storage device was a 6 L SUMMA® canister attached with the following Swagelok® fittings (Raleigh Valve and Fitting, Raleigh, NC): a union tee, an automatic tube weld (ATW) reducing union, a diaphragm valve, a plug valve, a Crawford special adaptor, a reducer, a female branch tee, two hose connectors and two nuts (fig. 1). Table A1, in appendix A, gives a description of the end connections, part numbers and procedure B1, in appendix B, describes the detailed procedure for building this device. The branch of the Swagelok® female tee was designed to connect to the gas collector and the other branch of the tee was designed to connect to a Swagelok® plug valve and Precision Scientific high vacuum pump (Belt Drive Model D-150, Winchester, VA). This design enabled the storage device and the gas collector to connect with Nalgene™ vacuum tubing (PVC 180, Fisher Scientific, Atlanta, GA) and provide a closed system for transferring gas

between the two devices. The Precision Scientific high vacuum pump capable of pulling 29.9 in. of Hg, was used to evacuate the SUMMA® canister before storing a gas sample. An Ashcroft® vacuum gauge (industrial gauge, Grainger®, Raleigh, NC) was used to determine when the SUMMA® canister was evacuated to the pump's capacity. A 11 mm Supelco septum (gr-2 gray, Sigma-Aldrich, Supelco Inc, Bellefonte, PA) was inserted inside the Swagelok® Crawford special adaptor and screwed on the port connected to the Swagelok® union tee on the SUMMA® canister. Each SUMMA® canister was leak tested to verify gas samples could be stored without air contamination. Possible leaks can come from a broken valve or improperly attached Swagelok® Crawford special adaptor. The Swagelok® Crawford special adaptor should not be overly tightened or it will push and twist the septum inside the port on the canister and allow air to leak inside. The septum was also inspected before each use to make sure no cracks or holes were developing from needle punctures. Each SUMMA® canister was leak tested by rechecking the vacuum inside the canister after it remained evacuated (29.9 in. Hg) for at least 12 hrs. If the vacuum in the SUMMA® canister lowered in any degree the septum and its position was inspected again and the canister was retested. Once the vacuum in the SUMMA® canister remained constant at 29.9 in. of Hg, it could be used in the method for storing gas samples.

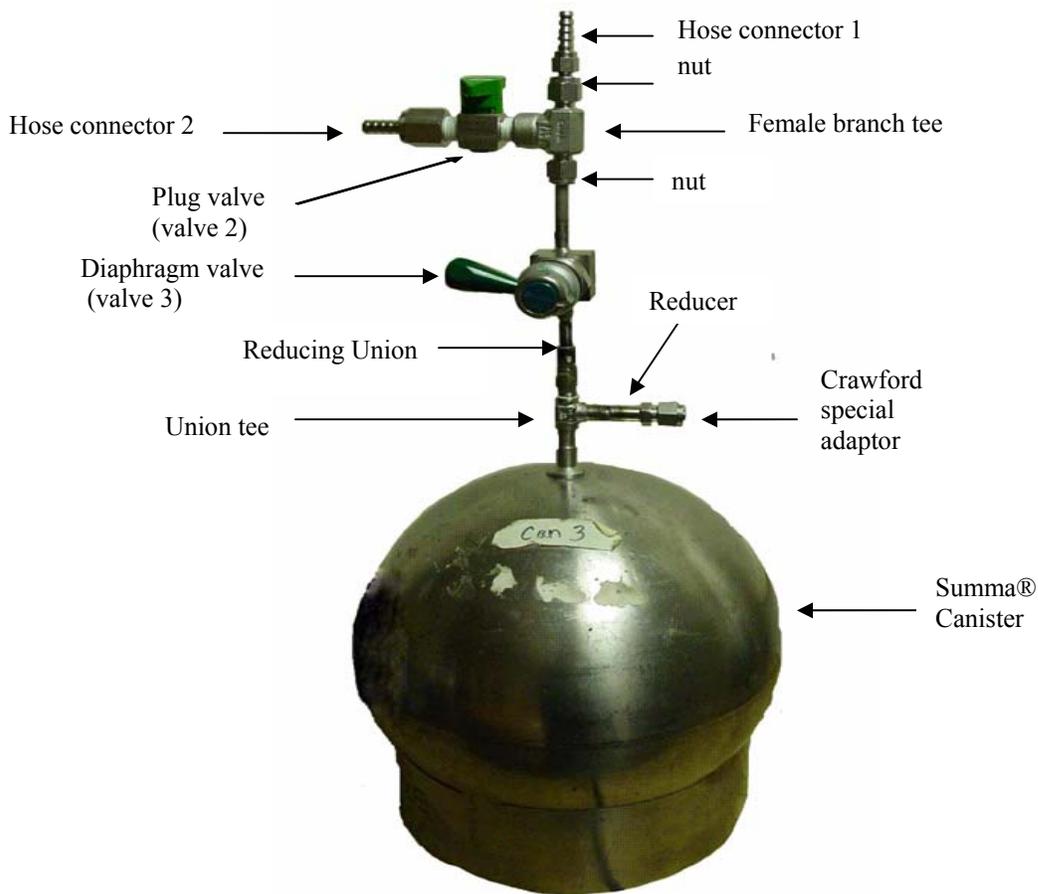


Figure 1. Summa Canister with Swagelok® fittings and valves

2.1 Testing Gas chromatography

Gas samples were analyzed using a Shimadzu 15-A gas chromatograph (GC) (Shimadzu Scientific Instruments, Inc., Norcross, GA). The GC was equipped with a thermal conductivity detector with a 3 m by 3.2 mm stainless steel column packed with 100/120 carbosieve SII. Ultra high purity (UHP) 100% helium (National Welders Supply Co., Raleigh, NC) was used as the carrier gas and entered the GC at a constant flow rate of 200 ml min⁻¹. The GC was tested for its ability to accurately analyze N₂ gas samples without air contamination. An air leak inside the GC would result in background N₂ and lead to

inaccurate measurements of N₂ in samples. The first test determined the background N₂ in the GC without a sample or needle injection. This test was referred to as a “system blank”. System blanks were done by physically blocking the injection port and performing normal analysis. The second test determined the amount of N₂ introduced into the GC by puncturing the septum with a syringe needle and performing normal analysis. This test was referred to as a “blank injection”. No gas sample was actually injected into the GC for this test. Standard gases used for calibration were run as samples to determine the GC’s percent recovery. These gases were composed of 50% N₂ / 4 % CH₄, 30% N₂/ 50% CH₄, 10% N₂/ 80% CH₄ (National Specialty Gases, Division of National Welders Supply Co. Inc., Raleigh, NC).

2.2 Testing Gas Collection Method

An experiment was done in a controlled laboratory environment to determine if the gas collection method could accurately and precisely collect and measure N₂ gas emissions from an open pond treatment system. The experiment involved simulating gas production in a lagoon by bubbling ultra high purity (UHP) helium gas (National Welders Supply Co., Raleigh, NC) in a tank filled with 80 liters of tap water and using the developed gas collection method to collect and analyze the gas (fig. 2).

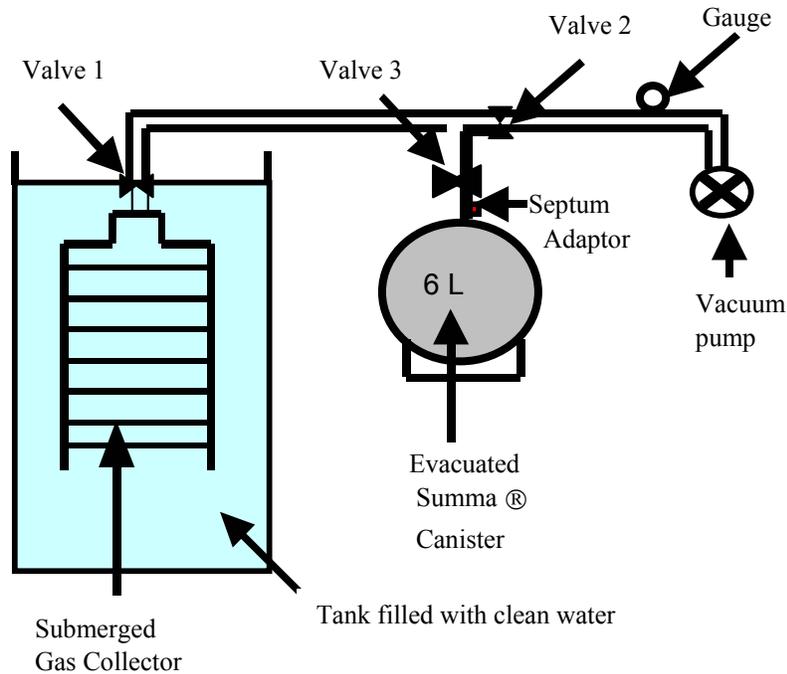


Figure 2. Diagram of experimental design for testing gas collection method

The experiment used water with dissolved oxygen concentrations lower than 10% saturation. The dissolved oxygen was removed by bubbling UHP helium gas through the water with a fine bubble diffuser (Point Four Systems Inc., model MBD 75, Richmond, BC, Canada) and Nalgene® vacuum tubing. The removal process of dissolved oxygen and dinitrogen by the helium bubbles was assumed to be the same, so the percent removal of dissolved oxygen and dinitrogen from saturated conditions should also be the same (Wold, 1973). In this experiment, the effect of dissolved N₂ stripping would be minimal because of the low dissolved dinitrogen concentrations in the water column. An accurate method should measure close to zero percent N₂ if no air leaked into the system. However, the amount of N₂ measured from the method would quantify the amount of N₂ introduced into the system from air contamination.

Water temperature was measured with a mercury thermometer and the atmospheric pressure was measured by a nearby weather station. Dissolved oxygen concentrations were measured with a Cole Parmer dissolved oxygen (DO) meter (WTW® Multiparameter Kit, Vernon Hills, IL) and a galvanic DO probe (WTW Cellox 325, Cole Parmer Instrument Co, Vernon Hills, IL) before and after every experiment. The gas collector, with valve one open, was placed upright in the tank filled with water (fig. 2), and submerged until valve one rested on the surface of the water. Valve one was then closed to avoid any air contamination. Approximately 10 liters of UHP helium gas was bubbled directly under the submerged gas collector using Nalgene® tubing. No diffuser was used to distribute the helium into the water. To transfer gas from the gas collector to an evacuated (29.9 in. of Hg) SUMMA® canister, both devices were connected with Nalgene® vacuum tubing and secured with Swagelok® hose clamps. Valve two was opened and the Precision Scientific high vacuum pump was used to evacuate the vacuum tubing to 29.9 in. of Hg. Valve two was closed before turning off the high vacuum pump. Valve one was opened and then valve three was slowly opened to allow the SUMMA® canister to fill (approximately six liters). The gas collector was pushed down into the tank until valve one touched the surface of the water and then valves three and one were closed. This slightly pressurized the SUMMA® canister and allowed gas samples to be taken from the septum-adapted nut with a syringe. A GASTIGHT® Hamilton syringe (samplelock™ 1005 SL, Sigma-Aldrich, Supelco Inc, Bellefonte, PA) was inserted in the Swagelok® Crawford special adaptor and was very slowly flushed five times before a sample was taken. The sample was then analyzed for dinitrogen gas by GC. Three samples were taken from each summa canister.

2.3 Testing to Estimate a Volumetric Mass Transfer Coefficient

Standard procedures established by the American Society of Civil Engineers (ASCE, 1992) were incorporated with the method developed by Wilhelms and Martin (1992) to estimate a bubble volumetric mass transfer coefficient, $[k_L a]_{\text{bubble}}$, for determining the rate of dinitrogen stripping. The procedures established by the American Society of Civil Engineers (ASCE, 1992) were used to estimate a total oxygen volumetric mass transfer coefficient for air bubbles in clean water. In addition to this, the approach developed by Wilhelms and Martin (1992) was used to determine the bubble and surface oxygen volumetric mass transfer coefficients from the total oxygen volumetric mass transfer coefficient. The total volumetric mass transfer coefficient would not be useful in determining the rate of stripping because it would include the surface gas exchange. It should also be noted that these procedures were written for evaluating oxygen mass transfer coefficients for diffuser aeration systems and not for dinitrogen stripping. However, assuming the $\frac{1}{2}$ power relationship of diffusion coefficients in forced convection mass transfer, the $[k_L a]_{\text{bubble}}$ value of dinitrogen gas would be 94 % of that for oxygen gas (Cussler, 1997). Laboratory evaluations from Speece and Humenick (1973) also found the k_L of N_2 to be 89% of the k_L of oxygen. Previous researchers have used these ratios to model the mass transfer of dinitrogen and oxygen in aeration systems (Colt and Westers, 1982; DeMoyer et al., 2003). For this research, the ratio of 0.94 was used to estimate the dinitrogen value of $[k_L a]_{\text{bubble}}$ from the laboratory determined oxygen coefficient. Measuring dissolved oxygen over dissolved dinitrogen was desired because of the accuracy and reliability of dissolved oxygen meters over the complicated procedures to measure dissolved dinitrogen (Bouck, 1982; Clesceri et al., 1995; Martin et al., 1995; Swinnerton et al., 1962).

The experiment involved using a tank filled with 80 liters of clean water and a water column depth of 0.53 meters. Sodium sulfite and a cobalt catalyst were added to deoxygenate the water to 0.5 g m^{-3} of dissolved oxygen. The water was aerated with a fine bubble diffuser and every thirty seconds the dissolved oxygen was measured. Aeration continued until the water was fully saturated and in equilibrium with the atmosphere. Another experiment was done to determine the surface and bubble gas exchange. The water was deoxygenated again using sodium sulfate and a cobalt catalyst. UHP helium gas was bubbled through the water at the same gas flow rate as with the air pump. The dissolved oxygen was again measured every thirty seconds. The increase of dissolved oxygen in the water in this experiment was solely due to the oxygen absorbing at the surface. The helium was bubbled until the rate of oxygen stripped by the helium bubbles equaled the rate of oxygen absorbing at the surface and the dissolved oxygen concentration became constant. Water temperature was measured with a mercury thermometer before and after each experiment.

2.3.1 Calculations

The following equations from Wilhelms and Martin (1992) were used to determine the bubble and surface oxygen volumetric mass transfer coefficients from the total oxygen volumetric mass transfer coefficient. These equations assume that the hydrostatic pressure effects on the bubble are small and that the gas concentration inside the bubble did not change significantly. The gas transfer process that occurred while aerating with air bubbles over time can be broken into two parts: oxygen absorption at the water surface, and absorption from the air bubbles, which is described in equations 1, 2 and 3.

$$\frac{dC}{dt} = \left[\frac{\partial C}{\partial t} \right]_{bubble} + \left[\frac{\partial C}{\partial t} \right]_{surface} \quad (1)$$

$$\left[\frac{\partial C}{\partial t} \right]_{surface} = [k_L a]_{surface} (C_{s_atm} - C) \quad (2)$$

$$\left[\frac{\partial C}{\partial t} \right]_{bubble} = [k_L a]_{bubble} (C_{s_bubble} - C) \quad (3)$$

where

$$\frac{dC}{dt} = \text{rate of total mass transfer per unit liquid volume, (g m}^{-3} \text{ sec}^{-1}\text{);}$$

$$\left[\frac{\partial C}{\partial t} \right]_{bubble} = \text{rate of mass transfer through the surface of the bubble, (g m}^{-3} \text{ sec}^{-1}\text{);}$$

$$\left[\frac{\partial C}{\partial t} \right]_{surface} = \text{rate of mass transfer through the water surface, (g m}^{-3} \text{ sec}^{-1}\text{);}$$

$$[k_L a]_{surface} = \text{liquid volumetric mass transfer coefficient for oxygen transfer at the surface of the tank, (sec}^{-1}\text{);}$$

$$[k_L a]_{bubble} = \text{liquid volumetric mass transfer coefficient for oxygen transfer at the surface of the bubble, (sec}^{-1}\text{);}$$

$$C_s = \text{saturation concentration in equilibrium with a gas phase}$$

$$C_{s_atm} = \text{saturation concentration that is equilibrium with the atmospheric gas phase above the surface of the tank, (g m}^{-3}\text{);}$$

$$C_{s_bubble} = \text{saturation concentration at the surface of the bubble that is assumed to be in equilibrium with the bulk gas phase, (g m}^{-3}\text{);}$$

$$C = \text{the bulk solution concentration, (g m}^{-3}\text{).}$$

Equations 2 and 3 are substituted into equation 1 and then equation 1 is integrated from an initial C_i to a final C_f oxygen concentration from time equal to zero to a lapse time of t . The result is equation 4.

$$\frac{C_s - C_f}{C_s - C_i} = \exp[-([k_L a]_{bubble} + [k_L a]_{surface})t] = \exp[-[k_L a]_{total} t] \quad (4)$$

The gas transfer process that occurred while bubbling helium gas can also be broken down into two parts: oxygen absorption at the water surface and oxygen being stripped from the water by the helium bubbles, which is described in equations 1, 2 and 5.

$$\left[\frac{\partial C}{\partial t} \right]_{bubble} = -[k_L a]_{bubble} C \quad (5)$$

The coefficients can be evaluated when equilibrium is reached and dC/dt equals zero. The equilibrium value, C_e , from the helium test is substituted for C in equations 5, 2 and 1. The resulting proportion is shown.

$$\frac{[k_L a]_{surface}}{[k_L a]_{bubble}} = \frac{C_e}{C_{s_atm} - C_e} \quad (6)$$

The equilibrium concentration, C_e , is the dissolved oxygen concentration when steady state equilibrium occurs and the rate of stripped oxygen equals the rate of oxygen absorbed from the surface of the water. Equation 6 can be substituted into equation 4 to calculate the $[k_L a]_{surface}$ and the $[k_L a]_{bubble}$ from the $[k_L a]_{total}$. Once the $[k_L a]_{bubble}$ for oxygen is calculated, it is adjusted to a $[k_L a]_{bubble}$ for dinitrogen by multiplying by 0.94.

2.4 Field Implementation of Gas Collection Method

The third objective of this study was to design and demonstrate a simple and safe implementation of the gas collection method for measuring N_2 gas emissions from an open pond treatment system. An aluminum frame attached to a flotation board was used to keep

the gas collector secure and stable just below the surface of the lagoon (fig. 3). The aluminum frame was divided into two pieces. The bottom piece holds the gas collector when it is fully submerged in the lagoon and the top piece holds the gas collector when it has been filled with 21 liters of gas. Tabs were used to keep the gas collector inside the frame when it is fully submerged in the water and when the gas collector is full of gas. Similar tabs were also used for attaching the frame to the flotation board using stainless steel bolts, washers and wing nuts. Table A3, in appendix A, lists the materials to make the flotation device and procedure B3, in appendix B, gives a detailed procedure for building this device. The flotation board (0.76 m by 1.2 m) was composed of a piece of styrofoam blueboard (2 in. thick) with two fiberglass boards (1/8 in. thick) covering the top and the bottom. The fiberglass boards and the styrofoam board were attached with 1/4 in. galvanized bolts (3 1/2 in. length), 1/4 in. washers, and 1/4 in. nuts. A 330 mm hole was cut in the middle to allow the gas collector to easily rise as gas accumulated. A square notch (76 mm by 76 mm) was cut at the edge of the hole to allow the volume in the gas collector to be read at the water level. The volume markings on the gas collector were painted with Rust-olem® white spray paint. This was done to allow the gas volume to be read when the collector becomes dirty from the lagoon environment. Silicone sealant was applied around the base of the gas collector's lid to securely seal it and keep the device leak free. The gas collector was inserted inside the aluminum frame and flotation board and bolted together with 1/4 inch bolts (4 1/2 in. length, threaded all the way), 1/4 in. washers, and 1/4 in. stainless steel wing nuts.

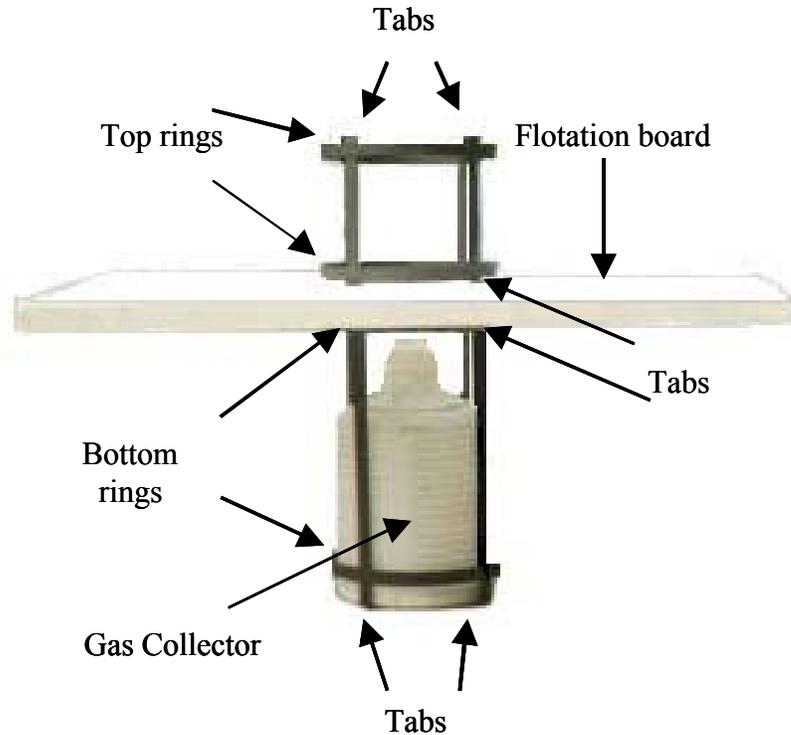


Figure 3. Device used to implement gas collection method

A nursery swine production unit located in Richlands, North Carolina, was selected as the site for implementing the gas collection method. The facility operated on a ‘pull-plug’ system with a cycle time of one week. After one week, the pits underneath the houses were emptied and the waste flowed by gravity into the lagoon treatment system (fig. 4). The lagoon treatment system was divided by hanging baffles to create a small anaerobic section and a partially aerated section (fig. 4).

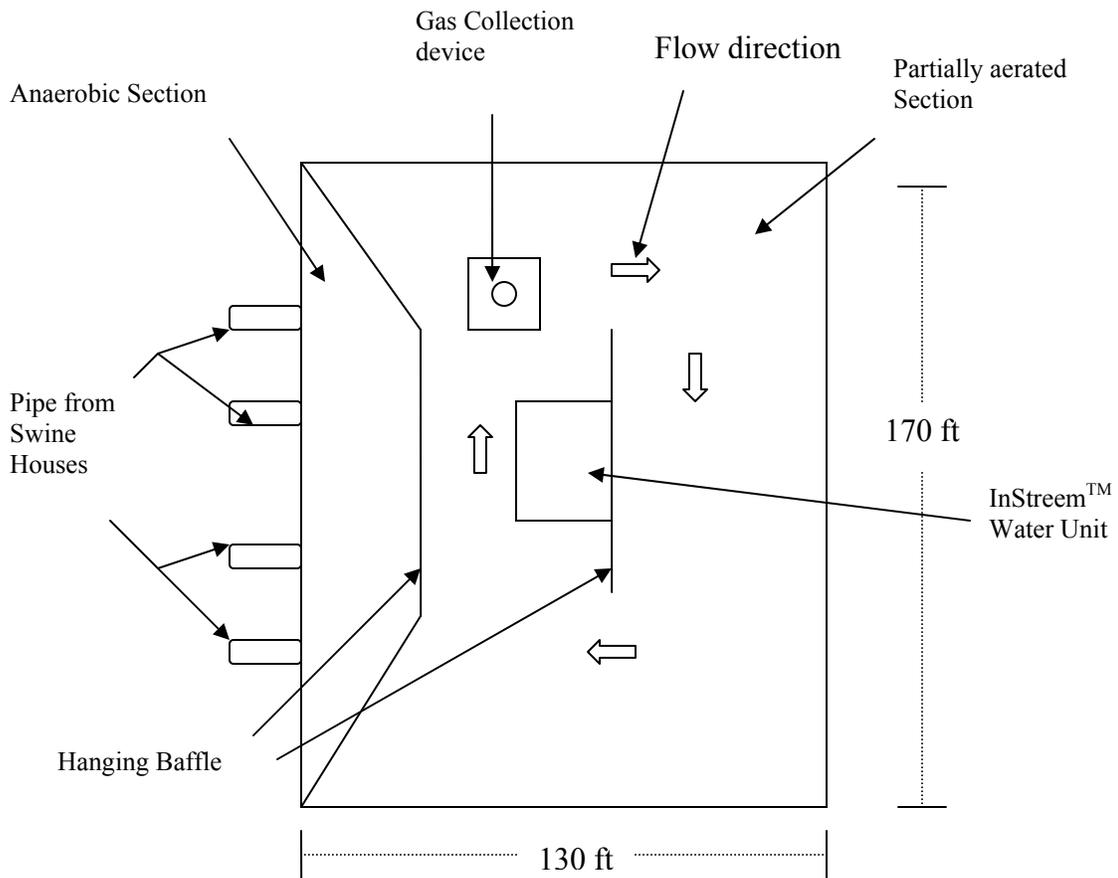


Figure 4. Diagram of lagoon treatment system with dimensions. Arrows inside the lagoon represent the flow direction.

Waste entered the partially aerated section at the bottom of the hanging baffle that separated the two sections. The partially aerated section contained an InStream™ Water Unit (IWU) and another hanging baffle. The IWU was designed and installed by Battelle Memorial Institute. The IWU provided mixing and dissolved oxygen by rotating nine 54 in. diameter discs that were submerged 21 inches into the water (see fig. D1 in appendix D). The disks were enclosed inside a metal chamber and mounted on pontoons (fig. 5).



Figure 5. InStream™ Water Unit installed in the lagoon treatment system

The hanging baffle in this section was used to allow the water to flow in a circular direction as shown in figure 4. The gas collection device was used to measure N_2 and methane production in the partially aerated section of the lagoon treatment system (fig. 6).



Figure 6 . Picture showing InStream™ Water Unit, gas collection device, and two hanging baffles

A weather station was installed at the site to monitor air temperature, wind speed, atmospheric pressure, and rain fall. Samples from the gas collection device were taken

weekly or biweekly depending on the length of time it took to fill the gas collector to at least 10 liters of gas. To transfer gas from the gas collector to an evacuated (29.9 in. of Hg) SUMMA® canister, both devices were connected with Nalgene® vacuum tubing and secured with Swagelok® hose clamps. Valve two (fig. 1) was opened and two 12-volt DC powered vacuum pumps (miniature diaphragm twin pump 15D, Gast® Manufacturing Inc., Benton-Harbor, MI; diaphragm pump N85.3, KNF Neuberger Inc., Trenton, NJ) connected in series were used to evacuate the vacuum tubing to 28 in of Hg. The two DC powered vacuum pumps were powered by a Champion® motorcycle power sport battery (Agri-supply, Raleigh, NC). Valve two was closed before turning off the DC powered vacuum pumps. Valve one was opened and then valve three was slowly opened to allow the SUMMA® canister to fill (approximately six liters). The gas collector was pushed down into the lagoon until valve one touched the surface of the water and then valves three and one were closed. The sample was then analyzed for dinitrogen and methane gas by GC. Gas analysis for each SUMMA® canister were run in triplicate.

2.4.1 Calculations

The average dinitrogen volumetric mass transfer coefficient estimated in the laboratory was adjusted for temperature, wastewater strength, and gas production rate to estimate the rate of stripping in the natural lagoon environment. Temperature has been shown to affect mass transfer coefficients of oxygen by the change in liquid viscosity (Mihelcic et al., 1993). Assuming that the change in viscosity would affect dinitrogen and oxygen mass transfer coefficients the same, a temperature adjustment was made by using the van't Hoff Arrhenius relationship. This relationship was approximated using the exponential function shown in equation 7 with a θ value of 1.024.

$$[k_L a]_{20} = [k_L a]_T \theta^{20-T} \quad (7)$$

where

$[k_L a]_T$ = the volumetric mass transfer coefficient at some actual temperature, T (°C);

$[k_L a]_{20}$ = the volumetric mass transfer coefficient at 20 °C.

Wastewater strength will also influence the mass transfer coefficient because of the presence of solids and surfactants (Baker, et al., 1975; Mihelcic et al., 1993). The mass transfer coefficient is corrected by using an alpha factor (equation 8).

$$\alpha = \frac{[k_L a]_{\text{process water}}}{[k_L a]_{\text{clean water}}} \quad (8)$$

Previous researchers have reported alpha values for different types of aeration devices and various wastewater strengths (Bass and Shell, 1977; Hwang and Stenstrom, 1985; Stenstrom and Gilbert, 1981; U.S. EPA, 1989). Values of alpha for oxygen have been reported to range from 0.4 to 0.9 in fine-bubble diffusers systems with mixed liquor domestic wastewater (Hwang and Stenstrom, 1985). The alpha values were found to increase with increasing treatment. Alpha factors also decreased with increasing airflow rate and increasing mixed liquor depth. The alpha factors ranged from 0.6 to 0.9 at a mixed liquor depth of 1.5 m, which would be similar to a lagoon treatment system. Other researchers have reported that alpha values of oxygen decreased from 0.9 to 0.4 when the total solids concentration of poultry waste increased from 1% to 5.5% in an oxidation ditch using cage rotors (Baker et al., 1975). After looking at the trends of previous research and assuming that the ratio of $k_L a$ for oxygen and dinitrogen are unaffected by wastewater strength, so that the same α value would apply, a range of alpha values of 0.6 to 0.8 were selected to correct the $k_L a$ for process wastewater in a swine waste treatment system.

The rate of gas production will also influence $k_L a$ values because at a higher gas flow rate more bubbles will be produced and therefore increase the interfacial area available for transfer. If the same bubble size and rise velocity occurs in both the field and the lab, the relationship of gas flow rates to the total specific areas and volumetric mass coefficients can be described using equation 9 (see appendix E-3 for calculation).

$$\frac{Q_{field}}{Q_{lab}} = \frac{a_{field}}{a_{lab}} = \frac{[k_L a]_{field}}{[k_L a]_{lab}} \quad (9)$$

where

- Q_{field} = gas production rate in a lagoon treatment system ($m^3 \text{ sec}^{-1}$);
- Q_{lab} = average gas flow rate used in experiment 2 ($m^3 \text{ sec}^{-1}$);
- a_{field} = total specific area (At/V) in field conditions ($m^2 m^{-3}$);
- a_{lab} = total specific area (At/V) in lab conditions ($m^2 m^{-3}$);
- At = total bubble surface area (m^2);
- V = total liquid volume (m^3).

While it is difficult to calculate total specific areas, a ratio of the gas production rate in an open pond treatment system to the average gas flow rate in the laboratory can be used to estimate the field volumetric mass transfer coefficient from the laboratory volumetric mass transfer coefficient. The dinitrogen bulk solution concentration, C, was estimated using an air solubility concentration table developed by Colt (1984) with the appropriate liquid field temperature and salinity value of 5 ppt. The dinitrogen concentration at the surface of the bubbles, C_{s_bubble} , was estimated by using Henry's law. The adjusted volumetric mass transfer coefficient, C and C_{s_bubble} were used to estimate the rate of dinitrogen stripped per unit liquid volume using equation 3. This rate was multiplied by the liquid depth to determine the rate of stripping per surface area under the carboy. The rate of biologically produced dinitrogen was estimated by subtracting the estimated rate of stripped dinitrogen from the total rate of N_2 measured with the gas collection method.

3.0 RESULTS AND DISCUSSION

3.1 Gas Chromatography

The gas chromatography testing revealed relatively little N₂ contamination. System blanks and blank injections measured 0.038 and 0.095 % N₂, respectively (Table 1). The standard deviation was higher than the average percent N₂ for the system blanks and blank injection. The coefficient of variation for this instrument at its detection limits would be close to 100%. These results reveal the instrument is at its detection limit for the blank and blank injection. The percent recoveries from calibration gases were 101% for 10% N₂, 100% for 30% N₂, and 98.4 % for 50% N₂. This indicates that the instrument calibration remained stable during measurement periods.

Table 1. Testing gas chromatography method^[a]

Sample	Percentage of N ₂ Average	Percentage of N ₂ Standard Deviation	Number of observations
System Blank ^[b]	0.038	0.068	15
Blank injection ^[c]	0.095	0.105	15
10% N ₂ / 80 % CH ₄ ^[d]	10.1	0.36	15
30% N ₂ / 50 % CH ₄ ^[d]	30.0	0.52	15
50% N ₂ / 4 % CH ₄ ^[d]	49.2	1.20	15

^[a] Testing to determine background N₂ and GC accuracy

^[b] Purge sample loop and injection port with helium

^[c] Penetrate septum with syringe needle with no sample injection

^[d] Standard gases

3.2 Gas Collection Method Testing

The first experiment was designed to test for air contamination by using the gas collection method to collect helium gas. To minimize the effect of stripping the dissolved oxygen and dinitrogen were lowered significantly. On average, the dissolved oxygen concentration was measured to be 0.80 g m⁻³ or 9.4 % oxygen saturation (Table 2). The helium gas samples analyzed by the GC were on average 0.57% N₂ (Table 2). This percent is the atmospheric

contamination associated with the sampling procedure. This value is consistent with the calculated detection limit for determining N₂ by using the standard deviation of the blank injection (Table 1) and adopting the standard convention that the detection limit is equal to 3 times the standard deviation plus the blank ($3 \times 0.105 \% + 0.095\% = 0.41\%$) when the number of observations is 8 or greater.

Table 2. Experiment 1: Results from testing gas collection method with initial low dissolved oxygen and dinitrogen concentrations for air contamination

Dissolved Oxygen (g m ⁻³) Average (std)	Dissolved N ₂ and O ₂ % Saturation Average (std)	% N ₂ Gas Measured from Collection Method Average (std)	Number of observations ^[a]
0.80 (0.11)	9.4 (1.2)	0.57 (0.097)	8

^[a] Gas samples were analyzed in triplicate.

3.3 Estimation of Mass Transfer Coefficient

This experiment involved bubbling air to oxygenate the water column from 0.5 g m⁻³ to an average saturation concentration, C_{s_atm} of 8.58 g m⁻³. This part of the experiment was replicated three times. The dissolved oxygen concentrations measured over time for the last replication are shown in figure 7. This experiment also involved bubbling helium gas through the water column. For this part the initial dissolved oxygen concentration was also 0.5 g m⁻³ and the final equilibrium dissolved oxygen concentration, C_e, was 1.43 g m⁻³. The dissolved oxygen concentrations measured over time are also shown in figure 7.

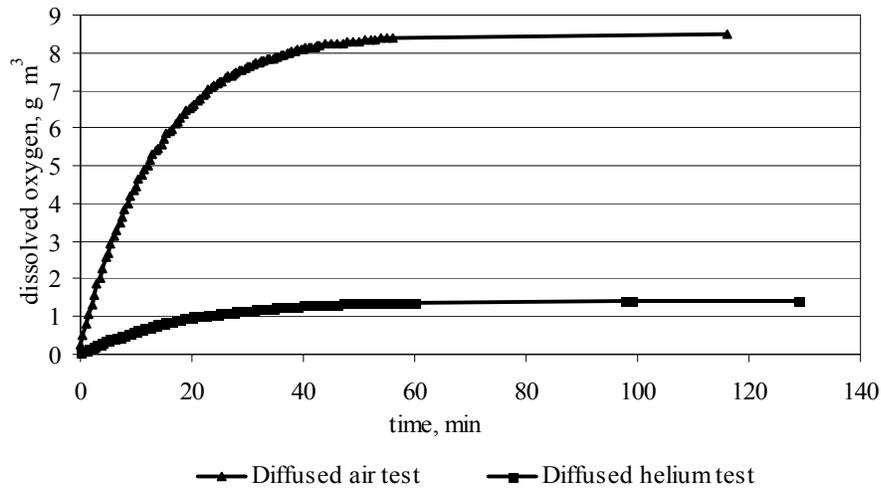


Figure 7. Dissolved oxygen measurements for diffused air and diffused helium in a tank filled with clean water.

A total volumetric mass transfer for oxygen was estimated using SAS® (2001), statistical software, with the nonlinear regression model described in ASCE (1992) and the dissolved oxygen measurements for the experiments using diffused air. The average total volumetric mass transfer coefficient, $[k_{La}]_{total}$ was calculated to be -4.13 hr^{-1} with a water temperature of 24.3 degrees Celsius. The average gas flow rate when bubbling helium and air was $2.0 \text{ liters min}^{-1}$. Equations 4 and 6 and the values for C_e and C_{s_atm} , were used to calculate $[k_{La}]_{bubble}$ from the $[k_{La}]_{total}$. This coefficient for oxygen was then adjusted by multiplying by the ratio of 0.94 to obtain the dinitrogen mass transfer coefficient. The resulting laboratory dinitrogen bubble volumetric mass transfer coefficient was calculated to be -2.93 hr^{-1} at $20 \text{ }^\circ\text{C}$.

3.4 Field Implementation of Gas Collection Method

Preliminary field data are reported to demonstrate the use of this method and the potential importance of N_2 stripping. The adjusted volumetric mass transfer coefficient, C and C_{s_bubble} were used to estimate the rate of dinitrogen stripped per unit liquid volume using equation 3. The liquid depth was multiplied by this rate to determine the rate of dinitrogen stripped per unit of surface area under the gas collector. The error associated with atmospheric contamination (0.57% N_2) found in the first experiment was subtracted from the total percent N_2 measured with the gas collection method. The rate of stripped N_2 was subtracted from the total rate of N_2 measured to estimate the rate of biologically produced N_2 . An average alpha value of 0.7 was used to estimate the dinitrogen volumetric mass transfer coefficient, which was used to calculate these rates during periods when the rotating disk aerator was off and on (fig. 8).

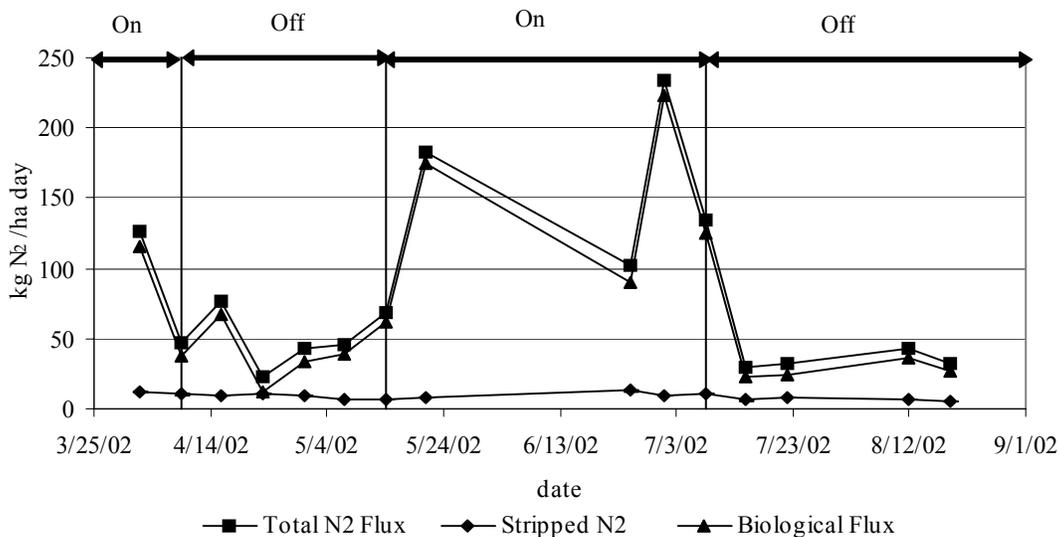


Figure 8. Dinitrogen flux measurements and stripping estimations using an alpha value of 0.7. Graph labeled when rotating disk aerator was on and off.

The total N₂ gas flux was significantly higher during the periods when the rotating disk aerator was on than when the aerator was off ($p = 0.0020$). However, the estimates of the flux due to stripping remained low regardless of the aeration status. The estimates of nitrogen flux due to biological activity, total flux minus flux due to stripping, were statistically different from zero when aeration was on and when aeration was off. When aeration was on, the average flux due to stripping was 10.5 kg N₂ ha⁻¹d⁻¹ out of a total average flux of 161 kg N₂ ha⁻¹d⁻¹, or 6.5% of the total nitrogen flux. However, when the aeration system was off, the average flux of stripped dinitrogen was 7.86 kg N₂ ha⁻¹d⁻¹ out of a total flux of 40.45 kg N₂ ha⁻¹d⁻¹, or 19.4% of the total nitrogen flux. The data suggest that the consideration of the effect of gas stripping on nitrogen emissions may be quite significant.

Bubble size is an important component of the calculation of flux due to gas stripping because the ratio of surface area to volume is proportional to the reciprocal of the bubble diameter. For a given volume of gas production, total surface area will double if bubble diameter is reduced by half. A larger total surface area would enable more mass transfer to occur from the liquid to the bubbles, increasing the flux of stripped nitrogen. For example, if the bubble diameter with aeration on is half of that estimated in this work, the stripped nitrogen flux would double to 21 kg N₂ ha⁻¹d⁻¹ or 13% of the total flux. With aeration off, the stripped flux would be 15.7 kg N₂ ha⁻¹d⁻¹ or 38.8% of the total flux. Because of the potential for significant influence of bubble size on calculated emissions, future research is needed to address the actual range of bubble sizes in liquid wastewater treatment systems.

A positive linear relationship was found between the non-dinitrogen flux and the estimated stripped N_2 flux (fig. 9). The calculation method assumed that the transfer coefficient, k_{La} , was proportional to total gas flow. However, the relationship of stripped N_2 flux to total gas flux was not as good as that to non-dinitrogen flux because the transfer rate also depends on the concentration of N_2 inside the gas bubble. Based on the trend in figure 9, an open treatment system with a higher methane production may strip dissolved dinitrogen at higher rate until a dynamic equilibrium is established between dinitrogen leaving the system by stripping and dinitrogen entering the system from the atmosphere.

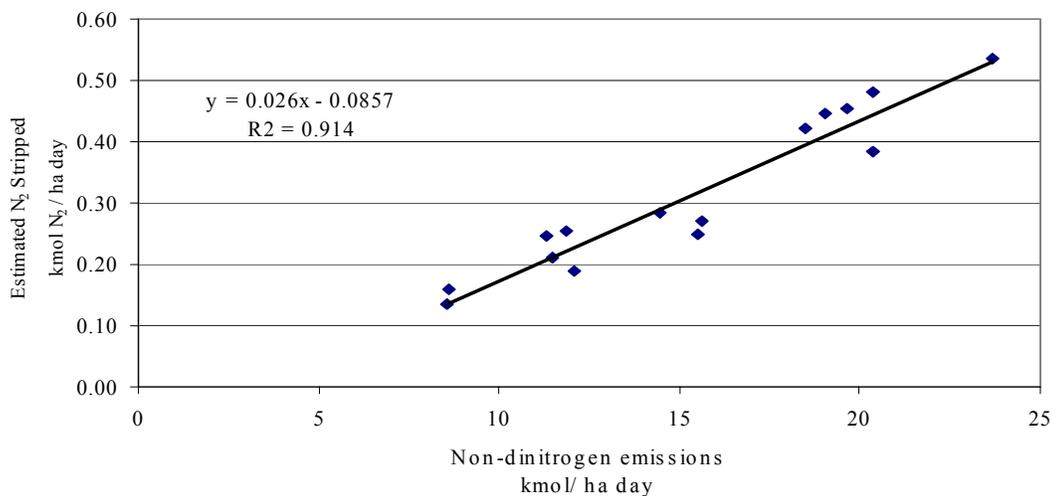


Figure 9. Relationship between estimated stripped N_2 flux when using an alpha value of 0.7 with measured non-dinitrogen flux.

Ammonia loss from animal waste systems is an important environmental concern. In order to properly implement abatement strategies, accurate estimates of the form and flux of nitrogen are needed. The method described above represents another tool to actually measure a form of nitrogen that is very difficult to measure and that has often been ignored. The method uses engineering procedures to address important complicating factors in the

measurement of N₂ emissions from open pond systems. The application of this method will enable more accurate estimates of farm-level nitrogen balances and, consequently, more accurate estimates of atmospheric losses of ammonia.

4.0 CONCLUSIONS

The developed gas collection method for measuring dinitrogen gas emissions from lagoon treatment systems was critically tested in a laboratory to ensure reliable dinitrogen gas measurements. The results from laboratory testing revealed that dinitrogen can be measured with low amounts of dinitrogen atmospheric contamination (0.57% N₂) when the method is done properly and when the equipment is functioning like it should. I found it is crucial to leak check the SUMMA® canisters prior to sampling and that the sealant on carboy lids be carefully monitored. The sealant on the carboy can be easily checked by filling the carboy with air, submerging it underwater and then checking for bubbles. If the lid is not properly sealed air bubbles will develop within a couple of seconds. This equipment needs close monitoring because any air leakage will give wrong measurements. The results from the gas chromatography testing revealed that the instrument was running in excellent condition and there was very little atmospheric N₂ in blanks (0.038% N₂), blank injections (0.105% N₂) and analysis of standard gases.

The volumetric mass transfer coefficient found in the laboratory for clean water was adjusted to compensate for field gas production rates, temperatures and wastewater quality to estimate the rate of stripped dinitrogen from the partially aerated lagoon. A major assumption in the estimation of stripping was same bubble sizes in the laboratory and in the field. The actual bubbles size may vary in the field and this will influence the significance of stripping. For example, a typical anaerobic lagoon with similar a bubble size as ours, stripping may contribute 19% of the total N₂ loss. If the bubble sizes doubles, the stripping may contribute

as much as 39% of the total N₂ loss. This is significant and should be considered when measuring for biological denitrification.

The results from implementing the method on a partially aerated swine waste treatment system suggested that N₂ was biologically produced from microbial denitrification at a rate higher than could be produced from stripping dissolved N₂. The total measured dinitrogen was also found to be significantly higher when aeration was on ($p=0.0020$) and was on average 161 kg N₂ ha⁻¹day⁻¹. When the aeration was off the average total measured dinitrogen flux was 40.4 kg N₂ ha⁻¹day⁻¹. Harper and Sharper (1998) reported dinitrogen emissions of 120.1 to 8.9 kg N₂ ha⁻¹ day⁻¹ for two anaerobic lagoons in North Carolina. The results from this study are higher than the dinitrogen emissions reported by Harper and Sharpe; however, this would be expected because the lagoon treatment system in this study was partially aerated and had more opportunity for microbial nitrification and denitrification. Harper and Sharpe also did not consider stripped dinitrogen to be apart of their flux measurements. The actual nitrogen loss from denitrification could be 20% to 40% less than what they have reported.

REFERENCES

- Aneja, V.P., B. Bunton, J.T. Walker, and B.P. Malik. (2001). Measurement and analysis of atmospheric ammonia emissions from anaerobic lagoons. *Atmospheric Environment*. 35: 1949-1958.
- ASCE. (1992). *Measurement of oxygen transfer in clean water*. 2nd ed. New York, NY.: ASCE.
- Baker, D. R, R. C. Loehr, and A. C. Anthonisen. (1975). Oxygen Transfer at High Solids Concentrations. *Journal the Environmental Engineering Division, Proceeding of the American Society of Civil Engineers*. 101: 759-774.
- Bass, S. J. and G. L. Shell. (1977). Evaluation of Oxygen Transfer Coefficients of Complex Wastewaters. In *Proceedings of the 32nd Industrial Waste Conference*. 953-967. Ann Arbor, Mic.: Ann Arbor Science.
- Bock, E., I. Schmidt, R. Stuvén and D. Zart. (1995). Nitrogen loss caused by denitrifying *Nitrosomonas* cells using ammonium or hydrogen as electron donor and nitrite as the electron acceptor. *Archives of Microbiology*. 163: 16-20.
- Bouck, G. R. (1982). Gasometer: An inexpensive device for continuous monitoring of dissolved gases and supersaturation. *Transactions of the American Fisheries Society*. 111: 505-516.
- Clesceri, L. S., A. E. Greenberg & R. R. Trussel. (1995). *Standard Methods for the Examination of Water and Wastewater*. 19 ed. 2810: Dissolved gas supersaturation .APHA, AWWA, WPCF.
- Crites, R., and G. Tchobanoglous. (1998). *Small and Decentralized Wastewater Management Systems*. Boston: McGraw-Hill.
- Colt, J., and H. Westers. (1982). Production of gas supersaturation by aeration. *Transactions of the American Fisheries Society*. 111: 342-360.
- Colt, J. (1984). *Computation of Dissolved Gas Concentrations in Water as Functions of Temperature, Salinity, and Pressure*. Bethesda, Maryland: American Fisheries Society Special Publications 14.

- Cussler E.L. (1997). *Diffusion: Mass transfer in fluid systems*, 2nd ed., Cambridge: Cambridge University Press.
- DeMoyer, C. D., E. L. Schierholz, J.S. Gulliver, and S. C. Wilhelms. (2003). Impact of bubble and free surface oxygen transfer on diffused aeration systems. *Water Research*. 37: 1890-1904.
- Goreau, T.J., W. A. Kaplan, S. C. Wofsy, M. B. McElroy, F. W. Valois and S. Watson. (1980). Production of NO₂ and N₂O by nitrifying bacteria at reduced concentrations of oxygen. *Applied and Environmental Microbiology*. 40(2): 526-532.
- Harper, L. A. and R. R. Sharpe. (1998). Ammonia emissions from swine waste lagoons in the southeastern U. S. coastal plains. USDA-ARS Agreement No. 58-6612-7M-022. Raleigh, NC.: North Carolina Dept. of Environmental and Natural Resources.
- Harvey, H. H. (1975). Gas disease in fishes- a review. In *Chemistry and Physics of Aqueous Gas Solutions*, 450-485. Princeton, New Jersey.: The Electrochemical Society.
- Hwang, H. J. and M. K. Stenstrom. (1985). Evaluation of fine-bubble alpha factors in near full-scale equipment. *Journal of the Water Pollution Control Federation*. 57(12): 1142-1151.
- Jetten, M. S. M., M. Strous, K. T. van de Pas-Schoonen, J. Schalk, U. G. J. M. van Dongen, A. A. van de Graaf, S. Logemann, G. Muyzer, M. C. M. van Loosdrecht and J.G. Kuenen. (1999). The anaerobic oxidation of ammonia. *FEMS Microbiology Reviews*. 22: 421-437.
- Jones, M. L., S. K. Liehr, J. J. Classen and W. Robarge. (2000). Mechanisms of dinitrogen gas formation in anaerobic lagoons. *Advances in Environmental Research*. 4: 133-139.
- Koelliker, J. K. and J. R. Miner. (1973). Desorption of ammonia from anaerobic lagoons. *Transactions of the ASAE*. 16 (1): 148-151.
- Mc Neil, C. L., B. D. Johnson, and D. M. Farmer. (1995). In-situ measurement of dissolved nitrogen and oxygen in the ocean. *Deep-Sea Research I*. 42 (5): 819-826.
- Martin, G. E., D. D. Snow, E. Kim, and R. F. Spalding. (1995). Simultaneous determination of argon and nitrogen. *Groundwater*. 33(5): 781-785.

- Mihelcic, J. R., C. R. Bailod and J. C. Crittenden. (1993). Estimation of VOC emissions from wastewater facilities by volatilization and stripping. *Journal of Air and Waste Association*. 43: 97-105.
- Mulder, A., A. A. van de Graaf, L. A. Roberston and J. G. Kuenen. (1995). Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. *FEMS Microbiology Ecology*. 16: 177-184.
- Phillips, J. (1995). Control and pollution prevention options for ammonia emissions. EPA Contract No. EPA-456/R-95-002. Research Triangle Park, NC.: U.S. Environmental Protection Agency.
- Poth, M. (1986). Dinitrogen production from nitrite by *Nitrosomonas* isolate. *Applied and Environmental Microbiology*. 52 (4): 957-959.
- SAS. (2001). SAS User's Guide: Statistics. Ver. 8.2. Cary, NC.: SAS Institute, Inc.
- Schmidt, I. and E. Bock. (1997). Anaerobic ammonia oxidation with nitrogen dioxide by *Nitrosomonas eutropha*. *Archives of Microbiology*. 167: 106-111.
- Speece R. E., and M. J. Humenick. (1973). Carbon dioxide stripping from oxygen activated sludge systems. *Journal of Water Pollution Control Federation*. 45 (3): 412-423
- Stenstrom, M. K., and R. G Gilbert. (1981). Effects of alpha, beta, and theta factor upon the design, specification and operation of aeration systems. *Water Research*. 15: 643-654.
- Swinnerton, J. W., V. J. Linnenbom, C. H. Cheek. (1962). Determination of dissolved gases in aqueous solutions by gas chromatography. *Analytical Chemistry*. 34(4): 483-485.
- Tchobanoglous, G. and F. Burton. (1991). *Wastewater Engineering*. New York, NY.: McGraw-Hill.
- U.S. EPA. (1989). *Design Manual: Fine Pore Aeration Systems*. EPA Contract No. EPA-625/1-89-023. Cincinnati, OH.: EPA. Center for Environmental Research and Development.
- van de Graaf, A. A., P. de Bruijn, L. A. Robertson, M. S. M. Jetten, and J. G. Kuenen. (1996). Autotrophic growth of anaerobic ammonium-oxidizing micro-organisms in a fluidized bed reactor. *Microbiology*. 142: 2187-2196.

Walker, J. T., V. P. Aneja, and D. A. Dickey. (2000). Atmospheric transport and wet deposition of ammonium in North Carolina. *Atmospheric Environment*. 34: 3407-3418.

Weiss, R. F. (1970). The solubility of nitrogen, oxygen, and argon in water and seawater. *Deep Sea Research*. 17: 721-735.

Wilhelms, S. C. and S.K. Martin. (1992). Gas transfer in diffused bubble plumes. In *Jennings SM and Bhowmilk NG, Eds. Hydraulic Engineering: saving a threatened resource-in search of solutions*, 317-322. New York, NY.: ASCE.

Wold, E. (1973). Surface agitators as a means to reduce nitrogen gas in hatchery water supply. *The Progressive Fish-Culturist*. 35 (3): 143-146.

APPENDIX A – PART NUMBERS AND MATERIALS TABLES

Table A1. Materials used to make the SUMMA® can devices used in this research

<i>Part Name</i>	<i>Part Number</i>	<i>Company or person</i>	<i>End connection or description</i>	<i>Cost \$</i>
Adjustable Hose Clamps	MS-HCC-8	Swagelok® Raleigh Valve and Fitting Co.	½ in. OD hoses	1.90
Automatic tube Weld (ATW) Reducing Union	316-6-ATW-6-4	Swagelok® Raleigh Valve and Fitting Co.	3/8 in. OD tube stub at one end and ¼ in. OD tube stub at the other.	13.60
Crawford Special Adaptor	SS-404-1-0001	Swagelok® Raleigh Valve and Fitting Co.	A ¼ in. nut adapted to fit a septum inside	7.20
DL series diaphragm valve (valve 3)	SS-DLS-4	Swagelok® Raleigh Valve and Fitting Co.	¼ in. tube fitting on both ends	144.70
Female branch tee:	SS-400-3-4TTF	Swagelok® Raleigh Valve and Fitting Co.	Identical tube stubs with ID = ¼ in. and female pipe with ¼ in. opening	23.70
Front and Back Ferrule	SS-403-1 SS-404-1	Swagelok® Raleigh Valve and Fitting Co.	¼ in. OD	0.73 0.65
Hose connector (1)	SS-4-HC-A-401	Swagelok® Raleigh Valve and Fitting Co.	¼ in. ID hose connector and ¼ in. tube adapter	7.20
Hose connector (2)	SS-4-HC-7-4	Swagelok® Raleigh Valve and Fitting Co.	¼ in. ID hose connector and ¼ in. female NPT taper thread end	10.80
Nut	SS-402-1	Swagelok® Raleigh Valve and Fitting Co.	¼ in. OD	1.40
Plug valve (valve 2)	SS-4P4T2	Swagelok® Raleigh Valve and Fitting Co.	¼ in. male American standard pipe thread (NPT) on both ends	36.50
Reducer	SS-400-R-6	Swagelok® Raleigh Valve and Fitting Co.	¼ in. OD tube stub on one end and 3/8 in. OD on the other end	6.70
Septums	20421	Sigma-Aldrich Supelco Inc.	gr-2 gray, 11mm	33.50 for one pack of 100 septums
Stainless seal kit for DL valve	SS-3DK-DS	Swagelok® Raleigh Valve and Fitting Co.	NA	5.50
SUMMA® canister	NA	Bob Seila	Top connection was a 3/8 in. OD union tee	free
Teflon® tape	19081506	Fisher Scientific	½ in. by 520 in.	1.51

Table A2. Materials used for the carboy device, not including the flotation device

Part Name	Part Number	Supply Company	End connection or description/size	Cost \$
Hose connector (1)	SS-4-HC-A-401	Swagelok® Raleigh Valve and Fitting Co.	¼ in. ID hose connector and ¼ in. tube adapter	7.20
Nalgene® Polycarbonate Clearboy™ Carboy	16101-186	VWR Scientific Products	21 Liter volume	326.68 for four
Nut (fastener)	NA	BAE research shop	¼ in.	Free
Outdoor Goop®	NA	Lowes®	NA	4.87
Plug Valve (1)	SS-4P4T	Swagelok® Raleigh Valve and Fitting Co.	¼ in. OD tube fittings both ends	42.00
Rubber washers	NA	Lowes®	7/16 by 1 by 1/16 in.	0.62 for two
Stainless Steel Bulk head reducer	SS-400-R1-4	Swagelok® Raleigh Valve and Fitting Co.	¼ in. OD tube stub connection on one end and ¼ in. tube fitting	10.40
silicone sealant	NA	Lowes®	NA	2.86

Table A3. Materials used for flotation device

Part Name and description	Dimensions	Company	Number per system	Cost \$
¼ in. thick, 1 in. wide aluminum: used for the tabs and side bars	Tabs: 2 in. long Short bar: 10 in. long Long bar: 20 in. long Total length: 14 ft per device	NCSU Research Shop	16 tabs 4 short bars, 4 long bars	
1/8 in. thick, 1 in. wide aluminum: used for the rings	13 in. diameter rings: 40.8 in. length aluminum piece	NCSU Research Shop	4 rings	
Blueboard Styrofoam	2 in. by 4 ft. by 8 ft	Hughes Supply. Inc.	2	20.00
Fiber glass boards		Lowes	1	25.00
galvanized bolts	¼ in. 4 ½ long	Lowes	4	0.33 each
galvanized bolts	¼ in. 3 ½ long	Lowes	8	0.29 each
galvanized nuts	¼ in	Lowes	12	0.07 each
Rustoe!™ Spray Paint	NA	Burke Brothers	1	4.23
stainless steel wing nuts	¼ in	NCSU Research Shop	4	free
stainless steel washers	¼ in.	Lowes	28	0.05 each

Table A4 . Other material / equipment that are not shown in tables A1, A2, and A3.

Part Name: description/model number	Part or catalog number	Supply Company	Dimensions or capacity	Cost \$
Hamilton samplelock™ syringe: 1005 SL	26286	Sigma-Aldrich Supleco Inc.	5-ml, 22 gauge	76.40
Belt Drive AC Powered Vacuum Pump: Model D 150	5122005	Precision Scientific	29.9 in. Hg max. vacuum, 150 LPM open flow	Borrowed from Roberto Munello
High Vacuum DC 12-volt powered pump: N85.3 DC	NA	KNF Neuberger Inc.	29.2 in. Hg max. vacuum, 5.5 LPM open flow	364.55
Nalgene® Vacuum tubing: PVC 180	14 176 6B	Fisher Scientific	¼ in. ID, 3/16 in wall thickness	32.69 for one box (10ft)
High Vacuum DC 12 volt powered pump: 15D 5150	NA	Gast® Manufacturing Inc.	25 in. Hg max. vacuum, 6 LPM open flow	?
Ashcroft® Industrial vacuum gauge	2C569	Grainger®	Max vacuum 30 inch Hg	46.95
16 in. tool box with metal latches	NA	Lowes	NA	7.96
Champion® DC Motorcycle power sport battery (12 volt)	40434	Agri Supply®	NA	21.76

Table A5. Supply company information

Company Name	Address	City, State, zip code	Phone number
Agri Supply®	409 Highway 70 East	Garner, NC, 27529	1-919-772-0865
Burke Brothers	5227 Hillsborough St.	Raleigh, NC, 27606	1-919-851-1211
Cole Parmer Instrument Co.	625 East Bunker Court.	Vernon Hills, IL, 60061-1844	1-800-323-4340
Fisher Scientific	NA	Atlantic, GA	
Gast® Manufacturing Inc.	2300 Highway M-139	Benton Harbor, MI, 49022	1-616-926-6171
Grainger®	4820 Signett Drive	Raleigh, NC, 27604	1-919-790-0888
Hughes Supply, Inc.	2111 New Hope Church Rd.	Raleigh, NC, 27604	1-919-872-6543
KNF Neuberger Inc.	Two Black Forest Road	Trenton, NJ, 08691-1810	1-609-890-8600
Lowes	1575 US HWY 70 West	Garner, NC, 27529	
National Specialty Gases	P.O Box 12013	Research Triangle Park, NC, 27709	1-919-544-3772
National Welders Supply Co.	4301 Capital Blvd.	Raleigh, NC, 27604-3497	1-919-876-6710
Point Four System, Inc.	100-13720 Mayfield Place	Richmond, BC, Canada, V6V 2EA	1-800-267-9936
Precision Scientific	170 Marcel Dr.	Winchester, VA, 22602	1-800-621-8820
Shimadzu Scientific Instruments, Inc.	3070 Business Park Drive, Suite H,	Norcross, GA, 30071	1-800-951-9167
Supelco Inc.		Bellefonte, PA, 16823	1-800-247-6628
Swagelok® Raleigh Valve and Fitting Co.	2621 Rowland Road	Raleigh, NC	1-919-878-8085
VWR Scientific Products, VWR International Inc.	P.O Box 640169	Pittsburgh, PA, 15264-0169	1-800-932-5000

APPENDIX B – DETAILED PROCEDURES

B-1 Procedure used to build the SUMMA® Canister devices

The SUMMA canisters® were donated from Bob Seila and were already mounted with a (3/8 in. OD) union tee. The following is a step by step procedure used to build the SUMMA® canister devices.

- 1) Weld the side bend of the union tee to the 3/8 in. OD tube stub end of the reducer (SS-400-R-6).
- 2) Weld the top bend of the union tee to the 3/8 in. OD end of the automatic tube weld (ATW) reducing union (316-6-ATW-6-4).
- 3) Remove the seals and other components found inside the diaphragm valve (SS-DLS-4). Follow the Swagelok® procedures found in stainless steel replacement kit for the DL valve (SS-3DK-DS).
- 4) Weld the top of the ATW reducing union (1/4 in. OD) to the bottom tube stub connection (1/4 in. OD) of the diaphragm valve (SS-DLS-4).
- 5) Weld a (1/4 inch OD) stainless tube pipe, about 1 inch in length, to the top tube stub connection of the diaphragm valve.
- 6) Attach a 1/4 in. OD nut (SS-402-1) using both the front (SS-403-1) and back (SS-404-1) ferrules to the 1/4 in. OD tube pipe. For detailed directions for this contact your Swagelok® supplier.
- 7) Tightly screw the female branch tee (SS-400-3-4TTF) inside the 1/4 in. OD nut from one of the 1/4 tube stub connections of the tee.
- 8) Wrap teflon® tape around the 1/4 in. NPT thread connection of the plug valve (valve 2, SS-4P4T2). Tightly screw the 1/4 in. male connection of the plug valve inside the 1/4 in. female connection of the tee.

- 9) Wrap teflon® tape around the other ¼ in. NPT thread connection of the plug valve.
Tightly screw the ¼ in. male connection of the plug valve inside the 1/4 in. female connection of the hose connector 2 (SS-4-HC-7-4).
- 10) Attach a ¼ in. OD nut (SS-402-1) using both the front (SS-403-1) and back (SS-404-1) ferrules to the ¼ in. OD tube pipe connection of the hose connector 1 (SS-4-HC-A-401).
- 11) Tightly screw this piece on the other ¼ in. tube stub connection of the female branch tee (SS-400-3-4TTF)
- 12) Since the old seals were removed from the diaphragm, new ones must be put back in. Replace the news seals using the stainless steel replacement kit for the DL valve (SS-3DK-DS).
- 13) Place a septum (Sigma-Aldrich, 20421) inside the crawford special adaptor (SS-404-1-0001). Screw the crawford special adaptor (SS-404-1-0001) onto the reducer (SS-400-R-6).

B-2 Procedure to assembly carboy lid, fittings and plug valve

- 1) Cut a 3/8 in. diameter hole in the center of the carboy lid. Use sand paper to roughen both the top and inside surface around the hole.
- 2) Place one rubber washer through the 1/4 in. OD tube stub end of the stainless steel bulk head reducer (SS-400-R1-4). Having the tube stub end down, place stainless steel bulk head reducer through the hole in the center of the carboy lid.
- 3) Place another rubber washer through the end of the 1/4 in. OD inside the lid. Tightly fasten with a stainless steel 1/4 in. nut.
- 4) Remove the 1/4 in. nut from the tube fitting end of the stainless steel bulk head reducer and attach the bottom tube fitting connection of the plug valve (1) (SS-4P4T).
- 5) Attach the 1/4 in. OD nut (SS-402-1) with the 1/4 in. tube connection of the hose connector 1 (SS-4-HC-A-401) and reattach to the top connection of the plug valve.
- 6) Generously apply the Outdoor Goop® around the base of the stainless steel bulk head reducer, around the entire area of the rubber washers and the area beside the washers and cap. Do this for both inside and top of the carboy lid. Let the Outdoor Goop® sit for 12 hours and harden. This step is extremely important because it protects against the carboy leaking!

B-3 Procedure to build flotation device

Aluminum frame: See Appendix F, for the drawings of the frame:

- 1) Cut the 1/8 in. thick, 1 in. wide aluminum into 4 pieces that are 41 inches long. Bend the aluminum pieces to make a circle and weld the two ends together. This will make 4 (13 in. diameter) rings.
- 2) Cut the 1/4 in. thick, 1 in. wide aluminum to make 16 (2 in. long) tabs. Continue to cut the 1/4 in. thick aluminum into 4 long bars (20 in. long) and 4 short bars (10 in. long).
- 3) Weld the tabs to each end of the bars. The top and bottom tabs will be positioned in the opposite direction (fig. B1). The short bars will make the top piece and the longer bars will make the bottom piece.

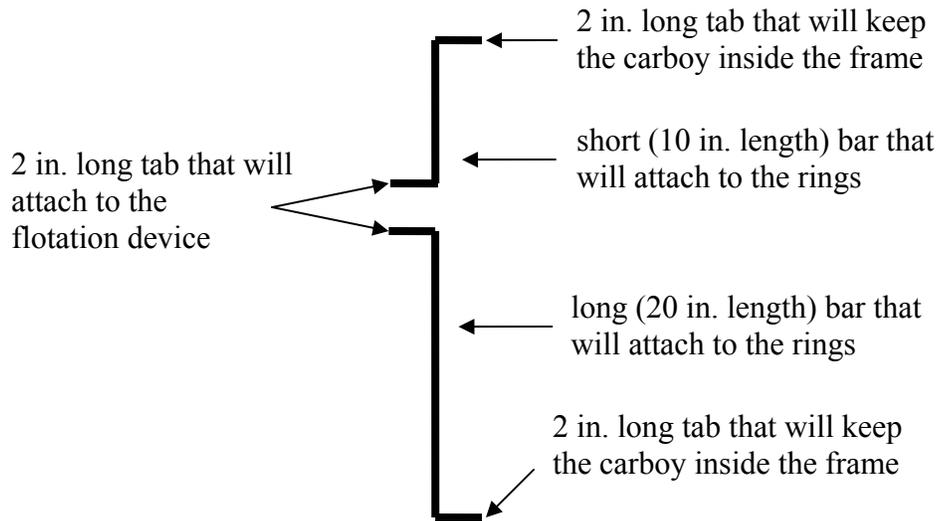


Figure B1. Diagram of aluminum bars and tabs used to build the flotation device

(not drawn to scale)

- 4) Weld the four short (top piece) bars inside two rings and the four longer bars inside the other two rings. When doing this, it is crucial to align the one bottom bar with a particular top bar because they will be bolted together. Mark each set (one top and one bottom) so you can remember when you do bolt them together. See the drawings for a diagram. For the tabs that will be used to bolt the flotation device, drill a $\frac{1}{4}$ in. diameter hole in the center of the tab. It is again very crucial to align the pairs together when doing this.

Building the flotation board

- 1) Cut the styrofoam blue board into one 30 in. by 48 in. (0.76 m by 1.2 m) rectangle. Cut two 30 in. by 48 in. (0.76 m by 1.2 m) rectangles with the fiber glass board.
- 2) Cut a 13 in. (330 mm) diameter circle in the middle of all three boards, making sure all three boards have the circle in the same place. Cut a square notch (76 mm by 76 mm) on one edge of the circle with all three boards.
- 3) Drill eight ($\frac{1}{4}$ in. diameter) holes along the edge of all the boards and 4 ($\frac{1}{4}$ in. diameter) holes along the edge of center (13 in. diameter) hole, also making sure each hole is aligned in the same place with all three boards (fig. B2). Use the $\frac{1}{4}$ in. bolts (3 $\frac{1}{2}$ in. length), $\frac{1}{4}$ in. washers, and $\frac{1}{4}$ in. nuts to fasten the board together. Place the carboy inside the bottom aluminum (20 in. length) frame. Use the $\frac{1}{4}$ in. bolts (4 $\frac{1}{2}$ in. length), $\frac{1}{4}$ in. washers, and $\frac{1}{4}$ in. wing nuts to fasten the boards and both bottom and top aluminum frames (fig. B3).

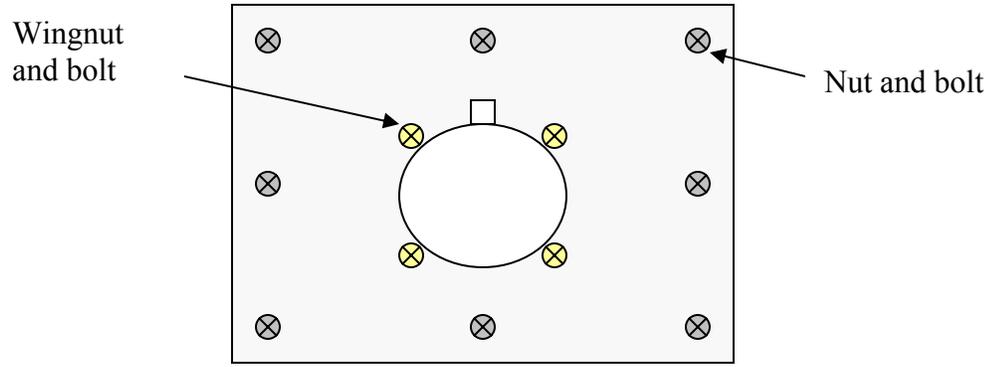


Figure B2. Diagram to show the top view of flotation device and the nuts and bolts locations.

Diagram is not drawn to scale.

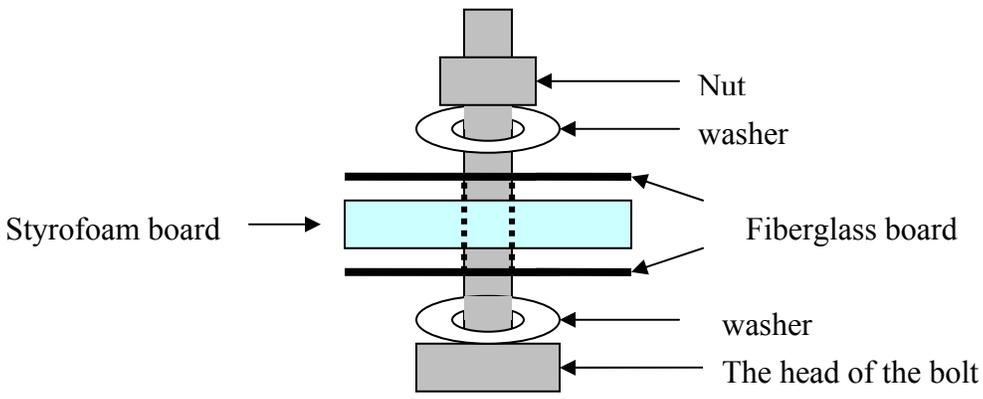


Figure B3. Diagram of styrofoam and fiberglass boards bolted together. Diagram is not drawn to scale.

APPENDIX C – DATA TABLES

Table C1. Dinitrogen and methane emissions from the lagoon treatment system

Date Collected	%N ₂ - 0.57%N ₂	% CH ₄	Pressure	Temp	Carboy Volume	Time	total Carboy	N ₂ Gas emission	CH ₄ Gas emissions
			atm	K	Liters	days	mols	kg N ₂ / (ha*d)	kg CH ₄ / (ha*d)
4/2/02	16.07	73.43	1.00	293	20	5	0.835	127	332
4/9/02	7.93	81.73	1.01	293	21	7	0.886	47.4	280
4/16/02	12.82	71.82	1.01	293	21	7	0.881	76.2	244
4/23/02	3.81	80.46	1.00	293	21	7	0.878	22.6	273
4/30/02	7.47	78.24	1.00	293	20.5	7	0.855	43.1	258
5/7/02	12.53	75.70	1.01	297	13	7	0.537	45.4	157
5/14/02	17.00	70.24	1.00	297	14.5	7	0.594	68.1	161
5/21/02	31.05	58.66	1.01	297	21	7	0.870	182	197
6/25/02	15.24	79.17	1.01	301	21	6	0.855	103	305
7/1/02	34.97	58.75	1.01	304	21	6	0.847	233	224
7/8/02	23.53	67.80	1.01	304	21	7	0.849	135	222
7/15/02	10.71	82.29	1.00	304	10	7	0.401	29.0	128
7/22/02	9.17	82.55	1.00	304	13	7	0.524	32.4	167
8/12/02	11.27	77.18	1.00	303	20	10	0.808	43.0	169
8/19/02	11.75	77.28	1.00	303	10	7	0.402	31.9	120

Table C2. Estimations of the stripped dinitrogen from field data and using an alpha valve of 0.7.

	Cs	C	Carboy Volume	Time	Gas Flowrate	(Field Ka) 20 oC temp	Field Ka field temp	Lagoon N ₂ in carboy	rate of stripped N ₂
Date Collected	g/m3	g/m3	Liters	days	m3/hr	1/hr	1/hr	mol	g/(m ³ hr)
4/2/02	3.02	14.67	20	5	1.667E-04	-2.85E-03	-2.81E-03	0.134	0.0328
4/9/02	1.49	14.67	21	7	1.250E-04	-2.14E-03	-2.11E-03	0.070	0.0278
4/16/02	2.41	14.67	21	7	1.250E-04	-2.14E-03	-2.11E-03	0.113	0.0259
4/23/02	0.72	14.67	21	7	1.250E-04	-2.14E-03	-2.11E-03	0.033	0.0294
4/30/02	1.40	14.67	20.5	7	1.220E-04	-2.08E-03	-2.06E-03	0.064	0.0273
5/7/02	2.20	13.67	13	7	7.738E-05	-1.32E-03	-1.44E-03	0.067	0.0165
5/14/02	2.98	13.67	14.5	7	8.631E-05	-1.47E-03	-1.61E-03	0.101	0.0172
5/21/02	5.44	13.67	21	7	1.250E-04	-2.14E-03	-2.33E-03	0.270	0.0191
6/25/02	2.46	12.6	21	6	1.458E-04	-2.49E-03	-3.02E-03	0.130	0.0306
7/1/02	5.47	12.21	21	6	1.458E-04	-2.49E-03	-3.23E-03	0.296	0.0217
7/8/02	3.68	12.21	21	7	1.250E-04	-2.14E-03	-2.77E-03	0.200	0.0236
7/15/02	1.68	12.21	10	7	5.952E-05	-1.02E-03	-1.32E-03	0.043	0.0139
7/22/02	1.44	12.21	13	7	7.738E-05	-1.32E-03	-1.71E-03	0.048	0.0184
8/12/02	1.79	12.4	20	10	8.333E-05	-1.42E-03	-1.80E-03	0.091	0.0191
8/19/02	1.87	12.4	10	7	5.952E-05	-1.02E-03	-1.29E-03	0.047	0.0135

Table C3. The estimated rate of stripping and biological emissions (using an alpha value of 0.7).

	rate of stripped N ₂	actual Liquid depth	Rate of Stripped N ₂	Biological N ₂	Total Gas emissions	Non-Nitrogen emissions
Date Collected	g/(m ³ hr)	m	kmol N ₂ / (ha day)	kmol N ₂ / (ha day)	total kmol / (ha day)	total kmol / (ha day)
4/2/02	0.03277	1.52	0.427	3.99	28.18	23.65
4/9/02	0.02781	1.52	0.362	1.24	21.35	19.66
4/16/02	0.02587	1.52	0.337	2.30	21.22	18.50
4/23/02	0.02945	1.52	0.383	0.33	21.16	20.35
4/30/02	0.02733	1.52	0.356	1.09	20.60	19.06
5/7/02	0.01652	1.68	0.238	1.38	12.93	11.31
5/14/02	0.01717	1.68	0.247	2.18	14.31	11.88
5/21/02	0.01914	1.68	0.275	6.22	20.96	14.45
6/25/02	0.03061	1.75	0.459	3.28	24.02	20.36
7/1/02	0.02173	1.83	0.341	8.07	23.80	15.48
7/8/02	0.02358	1.83	0.370	4.54	20.45	15.64
7/15/02	0.01387	1.83	0.217	0.88	9.66	8.63
7/22/02	0.01844	1.83	0.289	0.95	12.62	11.46
8/12/02	0.01910	1.52	0.249	1.35	13.62	12.09
8/19/02	0.01354	1.52	0.176	1.00	9.67	8.54

APPENDIX D - PICTURES

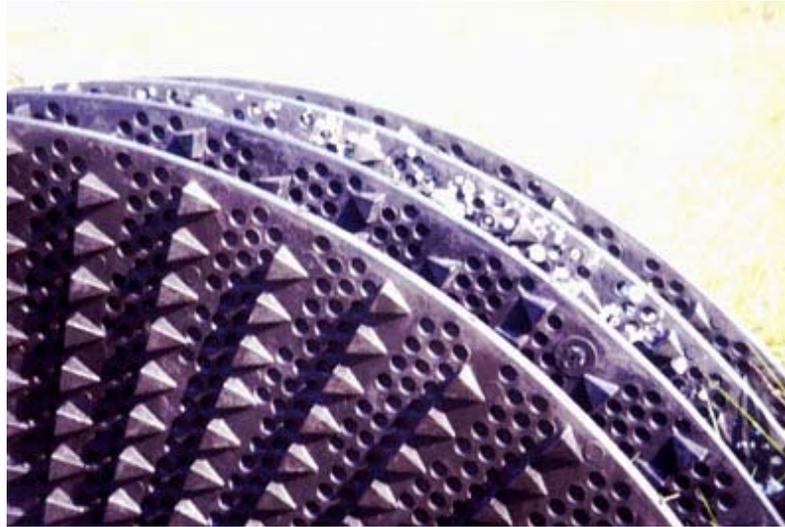


Figure D1. Disks inside the InStream™ Water Unit used in the lagoon treatment system



Figure D2. Picture of lagoon treatment system with InStream™ Water Unit and hog houses



Figure D3. Picture of Dr. Luna taking a sample from gas collector



Figure D4. Pigs inside hog house

APPENDIX E -CALCULATIONS

E-1 Calculations from the laboratory experiment

The following calculations were used to determine the $k_L a$ from the laboratory experiment.

$$\frac{C_s - C_f}{C_s - C_i} = \exp[-([k_L a]_{surface} + [k_L a]_{bubble})t] = \exp[-[k_L a]_{total} t] \quad (4)$$

$$\frac{[k_L a]_{surface}}{[k_L a]_{bubble}} = \frac{C_e}{C_{s_atm} - C_e} \quad (6)$$

The average total volumetric mass transfer coefficient, $[k_L a]_{total}$ was calculated to be - 4.13 hr^{-1} with a water temperature of 24.3 degrees Celsius. The saturation concentration, C_{s_atm} , was measured to be 8.58 g m^{-3} and the equilibrium concentration was found to be 1.43 g m^{-3} .

$$\frac{[k_L a]_{surface}}{[k_L a]_{bubble}} = \frac{C_e}{C_{s_atm} - C_e} = \frac{1.43}{8.58 - 1.43} = 0.20$$

$$[k_L a]_{surface} = 0.20 [k_L a]_{bubble}$$

$$0.20[k_L a]_{bubble} + [k_L a]_{bubble} = [k_L a]_{total} = -4.13$$

$$1.20[k_L a]_{bubble} = -4.13$$

$$[k_L a]_{bubble} = -3.44 \text{ hr}^{-1} \text{ for 24.3 degrees Celsius for oxygen}$$

$$[k_L a]_{bubble} = -3.44 \times 0.94 = 3.24 \text{ hr}^{-1} \text{ for 24.3 degrees Celsius for dinitrogen}$$

$$[k_L a]_{20} = [k_L a]_T \theta^{20-T} \quad (7)$$

$$\theta = 1.024$$

$$[k_L a]_{20} = 3.24 \times 1.024^{20-24.3} = 2.93 \text{ hr}^{-1} \text{ for 20 degrees Celsius}$$

E-2 Calculations from the field data

The mass transfer across the gas-liquid interface can be described using the two-film theory (Tchobanoglous and Burton, 1991). The two-film theory is based on a model that states two films exist at a gas-liquid interface (fig. E1) and at this two film interface, resistance will occur as gas molecules transfer between the bulk-liquid and the bulk-gaseous phase. For slightly soluble gases, like N_2 , the primary resistance is from the liquid film and the gas-phase resistance is ignored (Tchobanoglous and Burton, 1991).

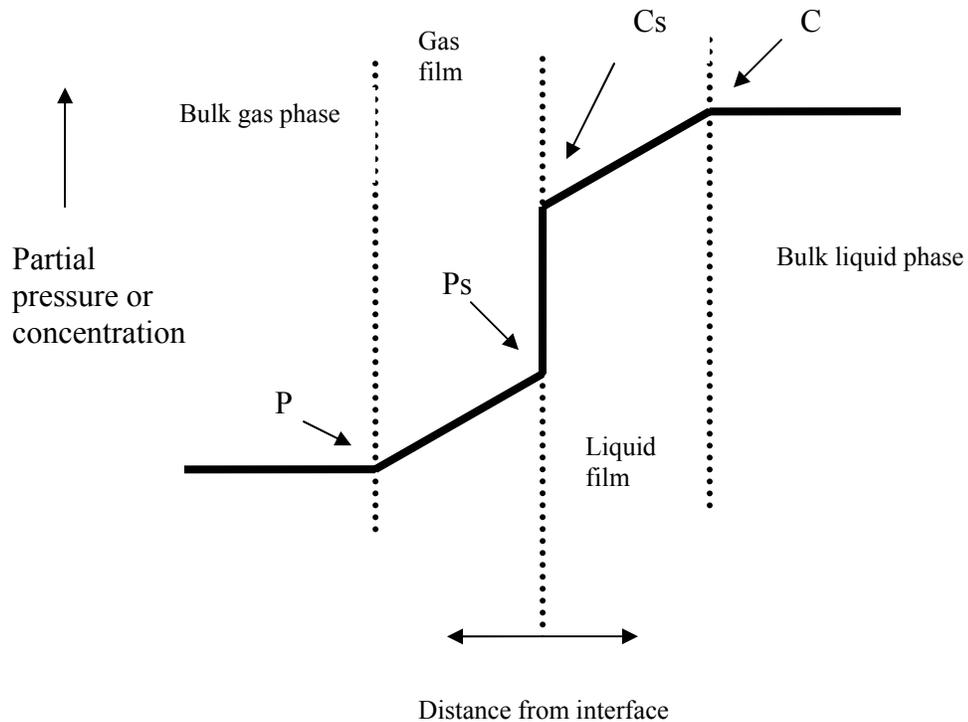


Figure E1. Diagram for the two-film theory for gas transfer

$$\left[\frac{\partial C}{\partial t} \right]_{bubble} = [k_L a]_{bubble} (C_{s_bubble} - C) \quad (3)$$

The dinitrogen bulk solution concentration, C, was estimated using an air solubility concentration table developed by Colt (1984) with the appropriate liquid field temperature and salinity value of 5 ppt. Equilibrium is assumed to occur across the interface of the bubble and Henry's law can be used to estimate C_{s_bubble} .

Henry's law: $P_i = HC_s$.

$$C_{s_bubble} = \frac{(\%N_2_measured - 0.57\%N_2)}{78\%} \times C$$

$$\text{Gas production rate (m}^3\text{/hr)} = \frac{\text{carboy_gas_volume(L)} \times \frac{1_m^3}{1000_L}}{\text{number_of_days} \times \frac{24_hr}{1_day}}$$

Adjust $[k_L a]_{bubble}$ using equations (7), (8), and (9).

$$\text{Mass transfer equation: } \left(\frac{g}{m^3 hr} \right) = [k_L a]_{bubble} (C_{s_bubble} - C)$$

$$\text{Rate of Stripped } N_2 \left(\frac{kmol_N_2}{ha_day} \right):$$

$$\left(\frac{g}{m^3 hr} \right) \times \text{liquid_depth(m)} \times \frac{10,000_m^2}{1_ha} \times \frac{1_N_2_mol}{28.02_g_N_2} \times \frac{1_kmol}{1000_mol}$$

Field emissions:

Ideal gas law:

$$\text{total mols in carboy} = \frac{\text{carboy_gas_volume(L)} \times \text{pressure(atm)}}{R \times \text{water_temperature(K)}}$$

$$\text{Gas constant } R = 0.08206 \text{ L atm / (mol K)}$$

% N₂ = % N₂ measured by GC – 0.57 % % N₂

note: 0.57 % N₂ was found to be air contamination from the procedure

$$N_2 \text{ mols in carboy} = \frac{\% \text{ } N_2 \times \text{total } \text{ mols}}{100}$$

Gas emission rate (kmol N₂ per ha per day) =

$$N_2 \text{ mols} \times \frac{1 \text{ kmol}}{1000 \text{ mols}} \times \frac{1}{0.0593 \text{ m}^2} \times \frac{10,000 \text{ m}^2}{1 \text{ ha}} \times \frac{1}{\text{number of days}}$$

Total gas emission rate (total carboy kmol per ha per day) =

$$\text{total carboy mols} \times \frac{1 \text{ kmol}}{1000 \text{ mols}} \times \frac{1}{0.0593 \text{ m}^2} \times \frac{10,000 \text{ m}^2}{1 \text{ ha}} \times \frac{1}{\text{number of days}}$$

Note: 0.0593 m² is the surface area underneath the carboy

Non-dinitrogen emission rate (non-dinitrogen kmol per ha per day) =

Total gas emission rate – dinitrogen emission rate

E-3 Sample calculation for equation (8)

$$\frac{Q_{field}}{Q_{lab}} = \frac{a_{field}}{a_{lab}} = \frac{[k_L a]_{field}}{[k_L a]_{lab}} \quad (8)$$

where:

- Q = gas production rate ($m^3 \text{ sec}^{-1}$);
- a = total specific area ($m^2 m^{-3}$);
- At = total bubble surface area (m^2);
- V_{liquid} = total liquid volume (m^3);
- d = depth of lagoon (m);
- SA_{liquid} = liquid surface area underneath carboy (m^2);
- D = bubble diameter (m);
- v = bubble rise velocity (m^2).

We assume the same bubble rise velocity and bubble diameter for the field and laboratory locations.

$$\text{Total specific area: } \frac{At}{V_{liquid}} = \frac{\text{total_bubble_surface_area}(m^2)}{\text{total_liquid_volume}(m^3)}$$

The surface area and volume of a bubble can be found using the following equations.

$$SA_{bubble} = \pi D^2 = \text{surface area of a bubble } (m^2)$$

$$V_{bubble} = \frac{\pi D^3}{6} = \text{volume of bubble } (m^3)$$

Divide the two equations together, the following relationship is found.

$$SA_{bubble} = \frac{6}{D} V_{bubble}$$

The total volume of bubbles in the water column can be written:

$$\text{Volume_bubbles} = Q \times \frac{d}{v} = \frac{m^3}{\text{sec}} \times m \times \frac{\text{sec}}{m}$$

$$total_SA_{bubble} = \frac{6}{D} \times Q \times \frac{d}{v}$$

$$Volume_liquid = SA_{liquid} \times d$$

$$a = \frac{At}{V_{liquid}} = \frac{Q \times \frac{d}{v} \times \frac{6}{D}}{SA_{liquid} \times d} = \frac{Q \times \frac{1}{v} \times \frac{6}{D}}{SA_{liquid}}$$

Based on the assumption that both locations have the same D , v , and SA_{liquid} , the remaining variables are $a = Q$. Equation 8 is based on this relationship: $a = Q$.

$$\frac{Q_{field}}{Q_{lab}} = \frac{a_{field}}{a_{lab}} = \frac{[k_L a]_{field}}{[k_L a]_{lab}} \quad (8)$$

Equation 8 can be used to calculate the field volumetric mass transfer coefficient from the laboratory coefficient and the field and lab gas flow rate.

$$[k_L a]_{field} = [k_L a]_{lab} \times \frac{Q_{field}}{Q_{lab}}$$

Appendix F – DRAWINGS

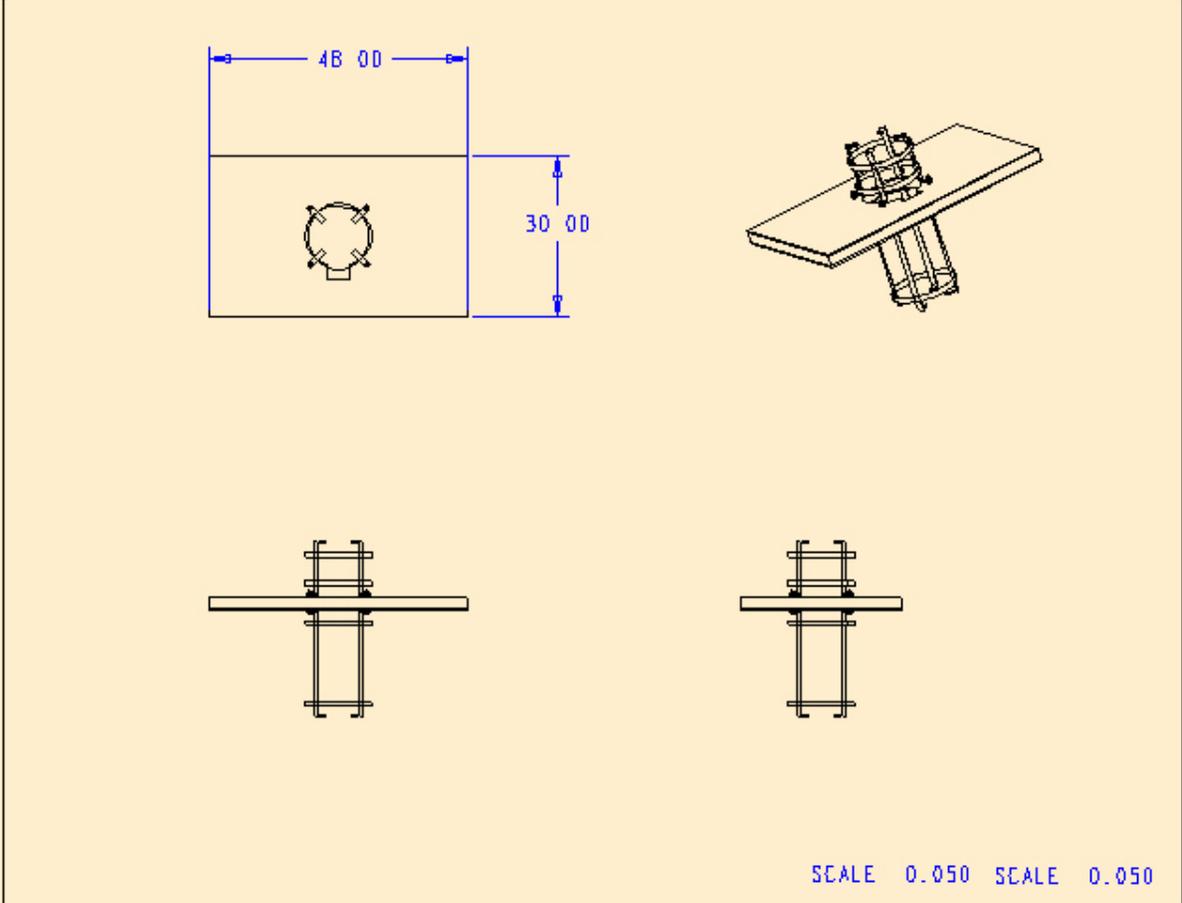


Figure F1. Drawing of carbony frame rotated to at an angle

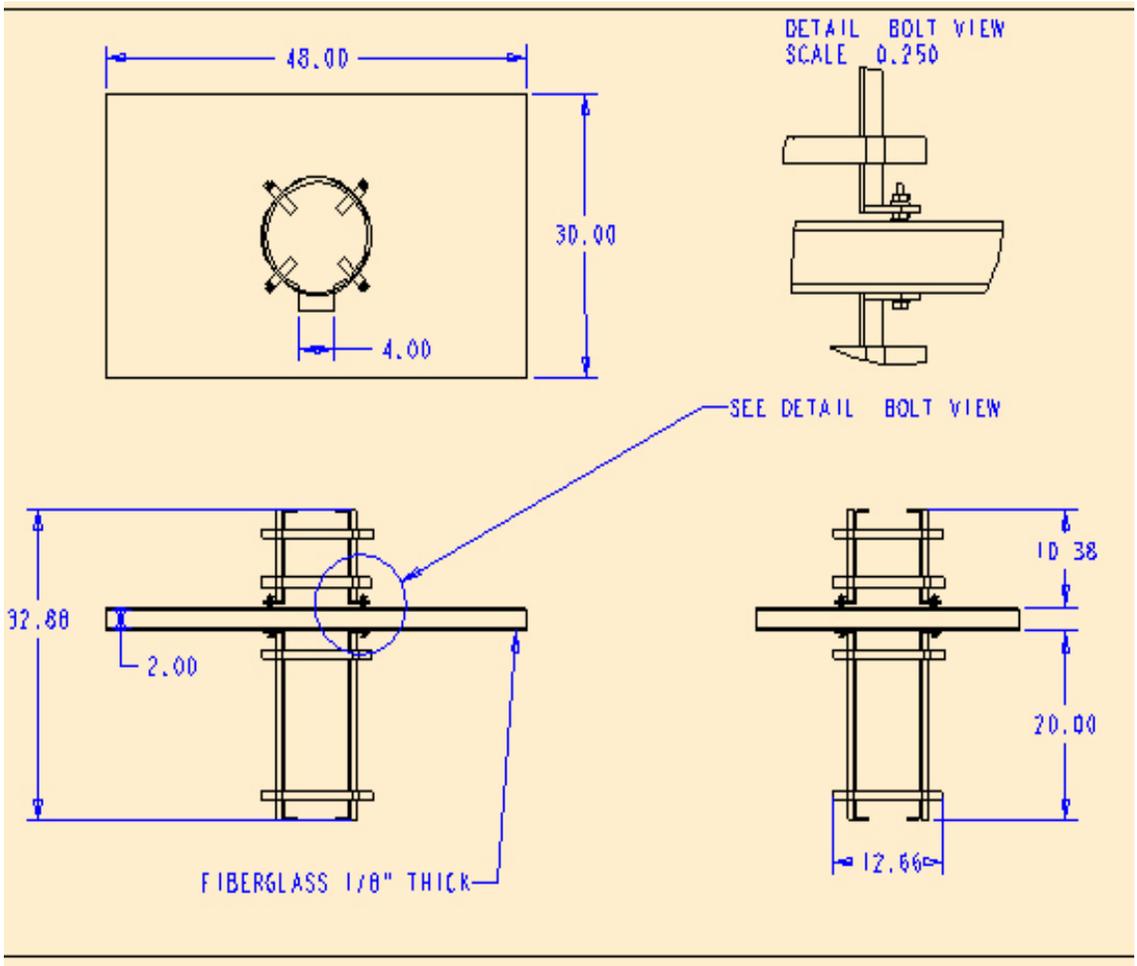


Figure F2. Drawing of carboy frame with dimensions and detailed bolt view