IN SITU OPTICAL SENSORS FOR MEASURING NITRATE IN FLORIDA WATERS

By

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LIST OF ABBREVIATIONS

ARL	Analytical Research Laboratory
CDOM	Colored dissolved organic matter
EPA	Environmental Protection Agency
N	Nitrogen
SUNA	Submersible Ultraviolet Nitrate Analyzer
SUNA V2	Submersible Ultraviolet Nitrate Analyzer Version 2
UV	Ultraviolet
WBL	Wetland Biogeochemistry Laboratory

CHAPTER 1
BACKGROUND AND OBJECTIVES

Nitrate in the environment

Similar to all systems on earth, the health of aquatic systems depend on a delicate balance between available energy and elements. The concept of ecological stoichiometry is defined by the specific ratio of essential elements in ecological systems (Frost et al., 2005). All systems operate with a specific ratio of carbon-to-nitrogen-to-phosphorus when in balance; when the stoichiometric ratio changes, the system becomes unbalanced.

A critical concern in aquatic systems is changes in nutrient stoichiometry causing nutrient limitation or nutrient enrichment. A nutrient (predominately nitrogen and phosphorus) is limiting in a system when the amount of that nutrient limits primary productivity (Liebig, 1855), leading to direct and indirect effects on ecosystem health and stability. Nutrient enrichment of the limiting element increases productivity, upsetting the balance between biological and chemical components and shifting ecosystem structure and function. The resulting eutrophication of aquatic systems can have drastic and long- lasting impacts on water quality, biogeochemical cycling, and community composition (Smith et al., 1999; Smith and Schindler, 2009). Eutrophication of surface waters can cause increased growth of algal biomass, decreased water clarity, decreased macrophyte vegetation, reduced species diversity, and depletion of dissolved oxygen (Smith, 2003). These visible effects of nutrient enrichment can abruptly and catastrophically shift species composition and ecosystem function (Smith and Schindler, 2009).

Growing concerns about the declining health of aquatic systems have prompted the development of novel methods for water quality analysis. Improved methods are needed for the detection and prediction of nutrient impairment before there are long-term effects. Instead of analyzing the stoichiometry of a single spatial and / or temporal point as traditional water sampling methods are designed, scientists are looking to increase the spatial and temporal resolution when monitoring nutrients to obtain an ecosystem scale perspective.

Finding the solution to complex environmental problems is reliant on understanding time-dependent dynamics of nutrients in aquatic systems. By monitoring nutrient loads at a fixed temporal scale, discrete sampling methods are potentially missing short-term event or seasonal trends in biogeochemical transformations and nutrient export. Flow from storm events totaling less than 20% of the time is estimated to be responsible for 80% of nutrient export from certain watersheds (Dalzell et al., 2007). To understand nitrate dynamics at the same temporal scale in which environmental conditions change, more sophisticated instruments are needed to report data at a rate equal to or greater than the rate of change. Higher resolution data can lead to improved interpretations about short-term processes affecting aquatic systems and improved management decisions to stimulate ecosystem health.

Optical nitrate sensors

Used for decades in wastewater monitoring (Rieger et al., 2008) and oceanographic applications (Johnson and Coletti, 2002), optical nitrate sensors have only recently been developed for use in freshwater aquatic systems (Pellerin et al., 2013). This current generation of optical nitrate sensors for freshwater systems arose from the initial design of Dr. Kenneth Johnson and Mr. Luke Coletti at the Monterey Bay

Aquarium Research Institute (Johnson and Coletti, 2002).

The optical sensors use ultraviolet (UV) absorption spectrum technology for real time direct measurement of nitrate in situ. The concept of UV absorbance of nitrate in a sensor is consistent with bench top UV spectrophotometry in a laboratory. A photometer in the sensor measures transmittance, the amount of incident light at a given wavelength that is transmitted through the solution to the detector. Transmittance (T) and absorbance (A) of the light passing through a solution are related logarithmically:

$$\mathrm{A} = 2 - \log_{10} \%\mathrm{T} \tag{1.1}$$

The absorbance measurements (A) can then be used to calculate the concentration (c) of an absorbing substance in solution by Beer's Law:

$$\mathrm{c} = \frac{\mathrm{A}}{\varepsilon * \mathrm{L}} \tag{1.2}$$

where ε is the molar absorptivity of the absorbing substance and L is the path length of light through the solution (Pellerin et al., 2013). Dissolved constituents attenuate light as it passes through the water sample. An increased path length causes a greater attenuation of the incident light (Figure 1-1). A sophisticated algorithm is then used to deconvolve absorption attributed to nitrate from absorption attributed to other compounds in the same wavelength range (including bromide and colored dissolved organic matter) or scattering from suspended particulates (Pellerin et al., 2013).

Several models of optical nitrate sensors with varying design components and specifications are commercially available. The sensors used in this investigation are the Submersible Ultraviolet Nitrate Analyzer (SUNA) with a 10mm path length and the SUNA V2 with a 5mm path length (Figure 1-2) (Satlantic Inc., Halifax, NS, Canada). Advantages of Satlantic's SUNA include the range of wavelengths measured (190-370 nm), the maximum sampling interval (1 second), and the lamp type and lifetime (deuterium, 900 hours). SUNA design and manufacturer-stated specifications for the two models used are stated in Table 1 (Satlantic, 2009).

When compared with the conventional method of sampling an aquatic system and measuring nitrate in the laboratory (Environmental Protection Agency Method 353.2), optical nitrate sensors are novel because they are designed to directly measure nitrate concentrations in situ, eliminating the need to sample a water body at a discrete temporal scale and analyze the sample in a laboratory. The method is chemical-free, requiring no costly or sensitive reagents in the field. The sensors are capable of measuring a large nitrate range and most instruments have the potential to extract additional optical information from the spectral range (Pellerin et al., 2013). With the recent development and increasing availability of these optical water quality sensors, scientists can begin to provide insight into complex ecosystem scale questions that were previously out of reach.

Objectives and hypotheses

Since the pioneering work of Johnson and Coletti (2002), optical nitrate sensors have been employed to study a variety of aquatic systems including: diurnal nitrate variability in a California river (Pellerin et al., 2009), diel nitrate trends in subtropical spring systems (Heffernan and Cohen, 2010), nitrate at different temporal scales in snowmelt driven streams (Pellerin et al., 2011), and eutrophication in Irish estuaries (O'Boyle et al., 2014). Despite increasing use of optical nitrate sensors, questions remain about the accuracy of the instruments in specific natural waters because of the difficulty of mitigating optical interferences. Florida's distinctive nutrient concerns and diverse natural systems offer a unique opportunity to investigate these questions.

The objective of this thesis is to compare in situ optical sensors with wet chemistry laboratory methods for measuring nitrate and offer recommendations for the use of these sensors in Florida waters. Chapter 2 will explore matrix effects in five natural waters representative of North Central Florida by comparing optical and wet chemical methods. Chapter 3 will focus on instrument path length effects when light absorbing and light scattering interferences are present.

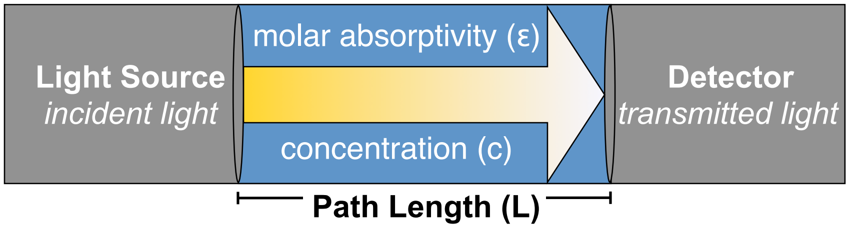

Figure 1-1. Conceptual diagram of attenuation in an optical nitrate sensor.

Figure 1-2. Submersible Ultraviolet Nitrate Analyzer (SUNA) with a 10mm sample path length (Satlantic Inc., Halifax, NS, Canada).

Table 1-1. SUNA Specifications for a 10mm path length instrument (Satlantic, 2011)

Path length:	10 mm	**Detection range:**	0.007 to 28 mg L^{-1} as N
Wavelength range:	190-370 nm	**Accuracy:**	± 0.028 mg L^{-1} or ± 10%
Lamp type:	Deuterium	**Precision:**	0.028 mg L^{-1} as N
Lamp lifetime:	900 hours	**Maximum sampling interval:**	1 second

CHAPTER 2
COMPARISION OF WET CHEMICAL LABORATORY AND IN SITU OPTICAL METHODOLOGY FOR THE MEASUREMENT OF NITRATE

Introduction

A standardized quality assurance and quality control protocol for optical nitrate sensor is not mandated as it is for laboratory methods. At this time, it is the responsibility of the researcher to evaluate the accuracy and precision of data collected with an optical sensor for the desired application. Current practices include pre-deployment sensor calibration, pre and post-use measurement of standard nitrate solutions, and validation with discrete samples analyzed analytically. Without these practices, the accuracy of the instrument is unknown and instrument bias can be present.

Calibration of the SUNA involves resetting the measurement baseline with ultrapure or deionized water. If the matrix of the desired natural water differs from the matrix of the ultrapure calibration water, the accuracy of the optical nitrate measurement can be affected. Matrix effects of natural waters are of principal concern when measuring nitrate in situ because there is no pretreatment of the natural water before it enters the instrument for measurement. Matrix effects include suspended particles that scatter light or dissolved constituents that absorb light, resulting in decreased accuracy due to reduced transmittance of light at wavelengths used in the algorithm to calculate nitrate. These matrix effects are vital to the quality of data produced from an optical sensor (Pellerin et al., 2013).

Conversely, the standard wet chemical method used to analyze discrete samples for comparison does alter the matrix of the natural water before measuring nitrate through filtration, dilution, and use of a dialyzer module. The standard wet chemical method used to analyze for nitrate in water and wastewater is EPA Method 353.2: Determination of nitrate-nitrite nitrogen by automated colorimetry (United States Environmental Protection Agency (USEPA), 1983). The method passes a filtered and preserved water sample through a cadmium column where nitrate in the sample is reduced to nitrite. The nitrite then reacts with a color reagent to form a red hue proportional to the original nitrate concentration. The intensity of the red hue is quantified by a spectrophotometer measuring the amount of light absorbed by the sample at a wavelength of 543nm. This measure of absorbance is lastly converted to the corresponding nitrate concentration using a standard curve, generated for each instrument run (USEPA, 1983).

This standard method includes many advantages to mitigate matrix effects. Water samples are filtered immediately following collection to remove suspended particles. At the time of analysis, interference from dissolved constituents can be lessened by sample dilution and use of a dialyzer module, a semipermeable membrane designed to separate the analyte from interfering substances in the matrix.

In this study, wet chemical laboratory methods for measuring nitrate were compared with in situ optical sensors in five aquatic systems representative of land uses and water chemistries in North Central Florida. The five sites selected embody unique matrix effects and include systems where nitrate concentrations from anthropogenic and natural sources are a concern. Specific objectives were to: 1) determine differences between nitrate measurements from a 10mm path length SUNA and two analytical laboratories on the University of Florida campus following EPA Method 353.2 and 2) determine differences between nitrate measurements from a 10mm path length SUNA, a 5mm path length SUNA, and an analytical laboratory following EPA Method 353.2 for each of the five study sites. Hypotheses were that low nitrate, low optical interference conditions would minimize the difference between the instruments and methods and that high nitrate, high matrix effect conditions will increase error associated with optical methods.

Materials and Methods

Study Sites

Five freshwater sites were selected to represent a range of land uses and water chemistries in North Central Florida where the application of optical sensors is desired (Figure 2-1). Ichetucknee Springs is a first magnitude spring that forms the border between Columbia and Suwannee County in Florida. The upper 3.5 miles of the 6-mile river is protected in the Ichetucknee Springs State Park. The site was selected to represent spring systems in Florida with low nitrate, low matrix effect natural water.

An isolated agricultural stream located perpendicular to NW 294th Avenue in Alachua County was selected to represent agricultural land uses in Florida with matrix effects associated with high nitrate concentrations. The study site was located downstream of The Holly Factory, a container nursery in Alachua County specializing in woody ornamentals, and upstream of the University of Florida Santa Fe River Ranch Beef Unit.

The Santa Fe River begins in Lake Santa Fe in eastern Alachua County and flows 72 miles to the Suwannee River in Branford County, Florida. The Santa Fe River is a blackwater system, rich in humic and fulvic acids with a characteristic tannic color.

The site was selected to represent blackwater systems present in many Florida rivers and wetlands where it is hypothesized that colored dissolved organic matter (CDOM) causes interference with optical measurements. The study site was located at the terminus of Boat Ramp Road in High Springs, Columbia County, Florida, downstream of the US 41 bridge.

Biven's Arm is a shallow, hypereutrophic lake in Alachua County. Sixty percent of the drainage basin is impervious, leading to high stormwater runoff inputs, excess nutrients, high productivity, and extensive algal growth (alachuacounty.us). Biven's Arm was selected to represent eutrophic and hypereutrophic lakes in Florida where extensive algal growth is a matrix effect of concern for optical sensors. The study site was located at a private residence on the southern side of the lake, accessed by SW 35th Place.

An urban stormwater stream located on the University of Florida campus in Alachua County was selected to represent the unique water chemistry of storm water systems including unpredictable turbidity and suspended sediment loads. The study site was located on the west side of Center Drive on the University of Florida campus and sampled under base flow conditions.

Field Analyses

Field measurements at the five study sites were collected on two separate occasions. The first experiment compared the standard wet chemical method performed by two different laboratories with optical measurements from a 10mm path length SUNA. The second experiment compared the wet chemical method from one laboratory with optical measurements from a 10mm path length SUNA and a 5mm path length SUNA.

For each experiment, all sites were sampled within 48 hours of each other to minimize changes in seasonal and environmental parameters. A Hydrolab multiprobe (Hach Company, Loveland, CO) was deployed at each site to measure water temperature, pH, conductivity, and dissolved oxygen to ensure consistency between sampling days. An ECO Triplet (Wetlabs, Philomath, OR) was deployed at each site to collect measurements of turbidity, chlorophyll-a, and colored dissolved organic matter to quantify possible matrix effects.

Fifty liters of site water was collected at each site to provide consistent subsamples for optical and chemical analysis. Seven polycarbonate vessels were set up in the field containing deionized water, natural site water, and natural site water with differing nitrate concentrations of 1 ppm, 3 ppm, 6 ppm, 12 ppm, and 18 ppm (from a 1000 ppm KNO_3 stock solution) to test matrix effects across a wide range of possible nitrate concentrations.

From these seven vessels, discrete grab samples were collected in triplicate, filtered with a 0.45 µm membrane filter, acidified to a pH < 2, and stored at < 4 degrees Celsius for analysis by the two analytical laboratories. Nitrate was measured optically with a 10mm path length SUNA for the first experiment and both a 10mm path length SUNA and 5mm path length SUNA for the second experiment. The SUNAs were operated in continuous mode for three minutes per sample. Nitrate measurements and full spectral data were logged for each sample using SUNACom software (Version 2).

Laboratory Analyses

Preserved water samples were analyzed for nitrate using USEPA Method 353.2 in the Wetland Biogeochemistry Laboratory (WBL) and the Analytical Research Laboratory (ARL) at the University of Florida in Gainesville, Florida. The Wetland Biogeochemistry Laboratory utilized an Auto-Analyzer with a 0-1 mg L^{-1} NO_3-N working range. Samples were diluted until the concentration was within range. The Analytical Research Laboratory utilized an OI Analytical autoanalyzer, a 3-30 mg L^{-1} NO_3-N working range, and a dialyzer module with a selectively permeable membrane to separate the analyte from interfering substances in the sample matrix.

Statistical Analyses

Statistical analyses were performed using JMP Version 11 (SAS Institute, Cary, NC). Tests of statistical significance between nitrate methods were conducted with the difference between known nitrate concentration and measured nitrate concentration as the response variable. Model effect variables included nitrate analysis method, known nitrate concentration, and the interaction effect between the two variables. A separate analysis was performed for each study site to assess each matrix effect. Comparisons of least-squares means and statistical significance were made using the Tukey test at an alpha level of 0.05.

Results and Discussion

Results from each method were compared at the different sites, separated by event. The first experiment with ARL, WBL, and SUNA 10mm is presented in Table 2-1 and the second experiment with ARL, SUNA 5mm, and SUNA 10mm is presented in Table 2-2. In Tables 2-1 and 2-2, p-values were used to determine significant difference between paired methods at each site. A p-value less than the alpha level of 0.05 indicated significant difference between the two methods. The differences between the known concentrations and the measured concentrations were used to determine accuracy of each method. A greater difference between known and measured nitrate concentrations (represented in Table 2-3 as least-square means) indicated a lower level of accuracy for the method at that specific site. The accuracy of the different methods across the range of matrix spikes is shown graphically for the first experiment in Figure 2-2 and the second experiment in Figure 2-3. Methods with a higher slope are indicative of lower accuracy. Across all sites and both experiments, higher nitrate concentrations resulted in decreased accuracy (shown by a higher difference value).

First Experiment

The first experiment compared the wet chemical analyses from the Wetland Biogeochemistry Laboratory and the Analytical Research Laboratory at the University of Florida and the optical analysis from a 10mm path length SUNA. At the eutrophic field site, nitrate measurements from the wet chemical method performed by the two laboratories were significantly different with a p-value <0.0001 (Table 2-1). As both laboratories used the same standard method (EPA Method 353.2), the significant difference in concentration can likely be attributed to the individual instruments. The Analytical Research Laboratory uses a dialyzer module before the sample is analyzed to remove dissolved constituents left in the matrix after filtering, shown as improved accuracy by a low least-square mean value in Table 2-3. Comparison between the ARL wet chemical method and the SUNA optical method produced a p-value <0.0001, showing a significant difference between the two methods. This difference can be attributed to extensive algal growth in the lake acting to scatter the light source. The comparison between the WBL wet chemical method and the SUNA optical method were not statistically different (p=0.386), indicating that matrix effects are a concern for both methods. When comparing least-square means for each method, only the ARL method (least squares mean = 0.336) differed from the SUNA method (0.866) and the WBL method (0.919) (Table 2-3).

At the agricultural field site, a method comparison mirrored the results from the eutrophic site; the ARL wet chemical method with the dialyzer module was significantly different from the other wet chemical method and the optical method (Table 2-3). A similar conclusion can be drawn, attributing the significant difference and decreased accuracy of nitrate measurements to matrix effects for the optical method (no filtering or dialyzer module) and the WBL wet chemical method (no dialyzer module).

At both the stormwater field site and the spring field site, all three methods when compared with each other were significantly different (Table 2-1). Least square means for the WBL, SUNA, and ARL methods at the stormwater site were 0.782, 0.416, and 0.125, respectively (Table 2-3). Least square means for the WBL, SUNA, and ARL methods at the spring site were 0.800, 0.530, and 0.108, respectively (Table 2-3). At both sites, there is an unspecified effect causing the methods to be significantly different from each other, and at this time, it is unclear if this difference can be credited to matrix effects or to an unknown variable.

No optical reading was obtained at the darkwater site due to optical extinction, where not enough incident light reached the detector for the SUNA to produce a reading (least square mean = 5.832). These findings contrast with specifications in the instrument user manual, where it is stated that CDOM concentrations in natural waters do not cause optical extinction (Satlantic, 2011). All three methods when compared with each other were significantly different with p-values <0.0001 (Table 2-1). In addition to producing the lowest accuracy of all the sites (optical extinction with the SUNA), the darkwater site produced the highest accuracy of any site and any method with the ARL wet chemical method (least mean square = 0.078), conceivably an effect of the dialyzer module removing interfering constituents before analysis.

Second Experiment

The second experiment compared the wet chemical analysis from the Analytical Research Laboratory and the optical analyses from a 5mm path length SUNA and a 10mm path length SUNA. When comparing p-values between methods, all combinations at all field sites were significantly different with the exception of three combinations (Table 2-2). The ARL wet chemical method and the SUNA 10mm method at the eutrophic and stormwater sites were not found to be different, a result not explained by the concept of matrix effects in combination with observed trends and requiring further analysis. The two optical methods, SUNA 5mm and SUNA 10mm, were not found to be different at the agricultural site, implying that with these specific matrix effects, path length had no influence. (Table 2-2). As in the first experiment, the 10mm SUNA did not record a nitrate concentration at the darkwater site because of optical extinction from CDOM. Interestingly, the SUNA with a reduced 5mm path length was able to measure nitrate at the darkwater site (least mean square=1.0928) despite an identical concentration of CDOM (Table 2-2). The influence of path length on mitigating optical interference will be investigated further in Chapter 3.

Conclusions

Matrix effects of light scattering and light absorbing substances are a concern when measuring nitrate with optical and wet chemical methods. Suspended substances including algal biomass and sediment will scatter incident light when using an optical sensor and produce a bias with the measurements. While attempts can be made to mitigate the effect of suspended particles by fitting an optical sensor with passive mechanisms (filters and guards) or actives mechanisms (mechanical wipes), discrete grab samples should be collected to ensure high quality data. Dissolved constituents pose a greater concern to optical sensor interference because the only mitigation available is algorithm correction for absorbance by these constituents. Visible substances including colored dissolved organic matter and unknown dissolved constituents in the sample matrix should be considered.

When measuring nitrate with wet chemical methods in the laboratory, the same matrix effects are of concern. In compliance with EPA Method 353.2, discrete water samples are filtered after collection and before analysis to remove suspended particles from contributing to measurement error. Diluting the sample or using a dialyzer module prior to analysis can mitigate matrix effects from dissolved constituents in the sample matrix. For the sample matrices tested, a dialyzer module (ARL method) was more effective at removing interference and increasing accuracy than dilution of the sample (WBL method), as seen in least-square means in Table 2-3.

The difference in accuracy between the two optical instruments with different path lengths is of interest and will be further explored in Chapter 3. This study has shown the importance of identifying possible matrix effects and selecting the method of nitrate analysis with the best form of interference mitigation.

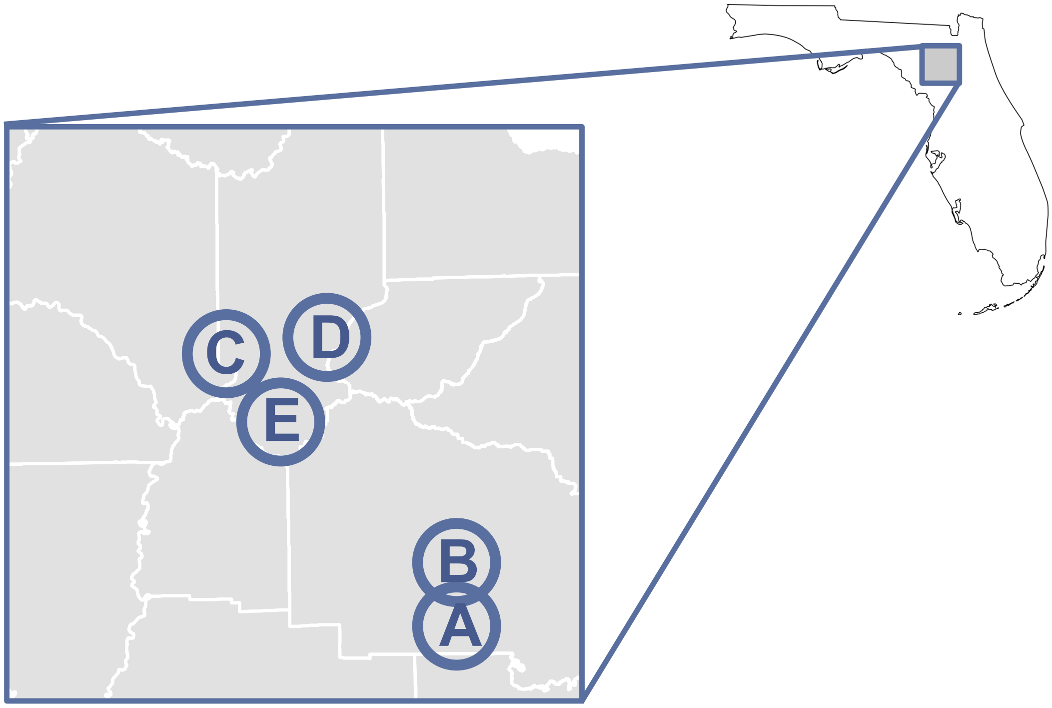

Figure 2-1. Study sites in North Central Florida. A) Biven's Arm - eutrophic system; B) stormwater site on the University of Florida campus; C) Ichetucknee Springs - spring system; D) agricultural system in Alachua County; E) Santa Fe River - darkwater system.

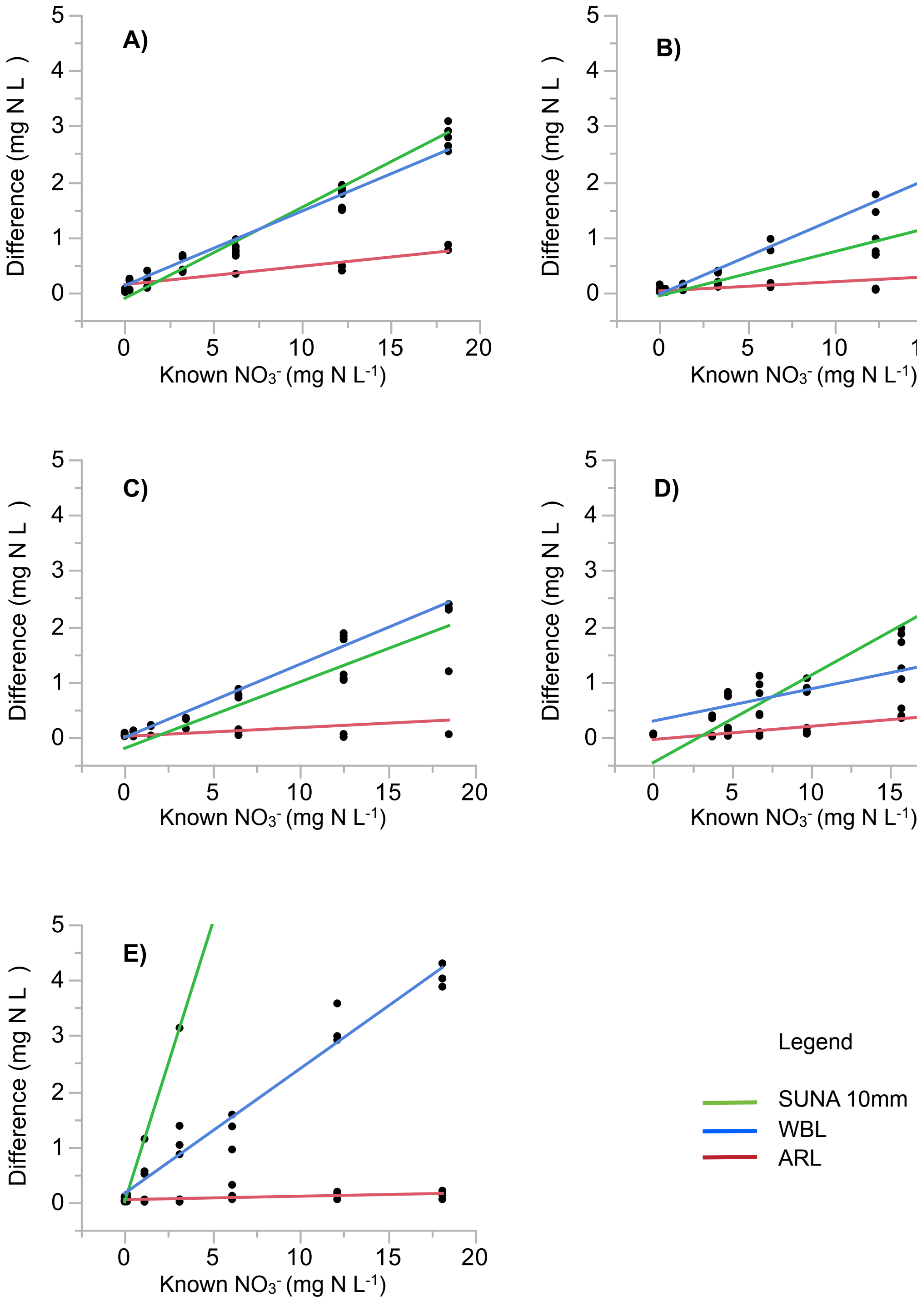

Figure 2-2. Comparison of method accuracy for Experiment 1, comparing the SUNA 10mm optical method, WBL wet chemical method, and ARL wet chemical method. Higher difference values indicate greater measurement error. Sites: A) eutrophic; B) stormwater; C) spring; D) agricultural; E) darkwater.

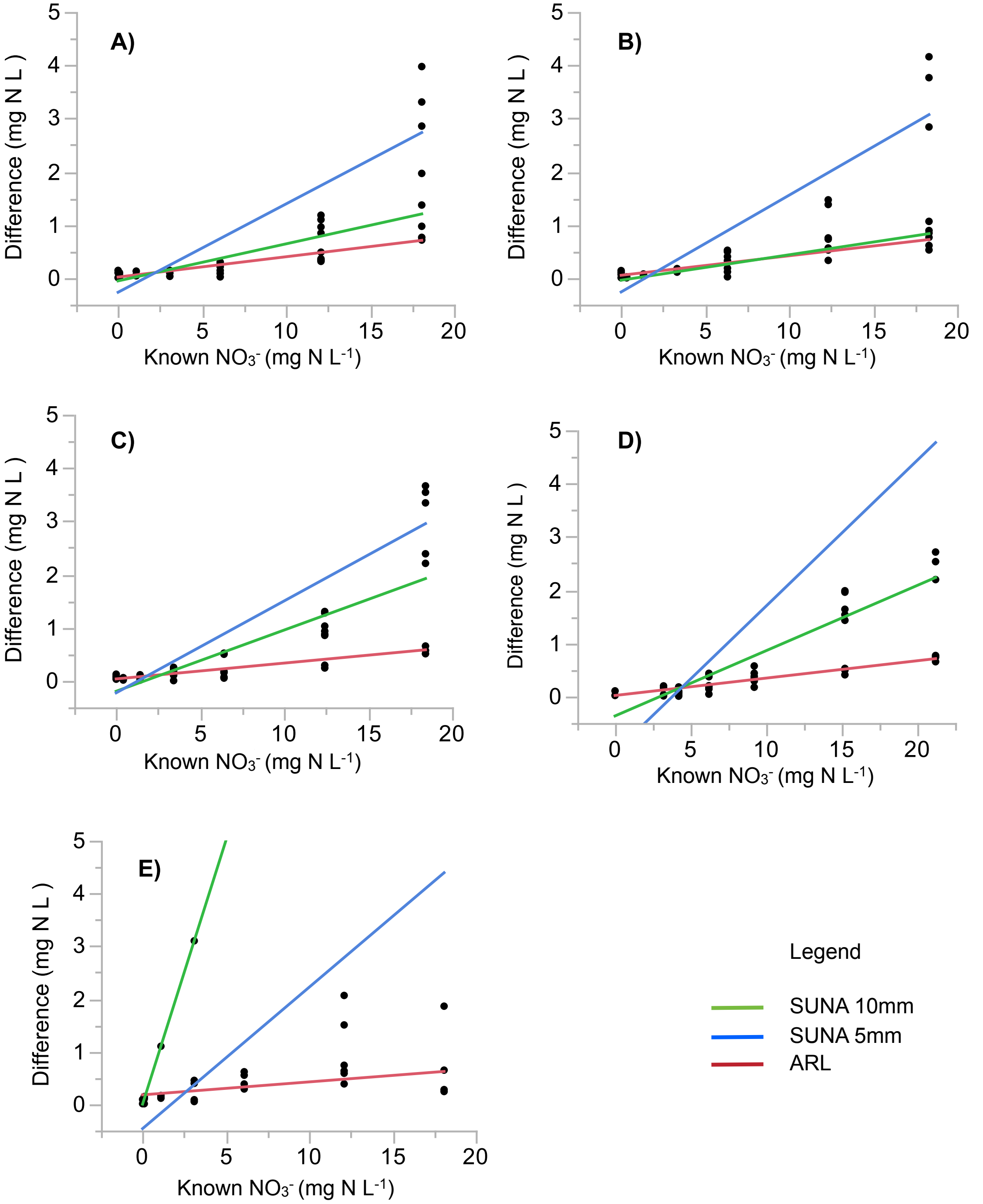

Figure 2-3. Comparison of method accuracy for Experiment 2, comparing the SUNA 10mm optical method, SUNA 5mm optical method, and ARL wet chemical method. Higher difference values indicate greater measurement error. Sites: A) eutrophic; B) stormwater; C) spring; D) agricultural; E) darkwater.

Table 2-1. Experiment 1, comparison between 10mm SUNA, WBL, and ARL nitrate measurement p-Values for paired method comparisons. p-Value < 0.05 indicates a significant difference between the two methods being compared.

Site	Method Comparison			p-Value
Eutrophic	ARL	vs.	SUNA	**< 0.0001**
	WBL	vs.	ARL	**< 0.0001**
	SUNA	vs.	WBL	0.3855
Stormwater	ARL	vs.	SUNA	**< 0.0001**
	WBL	vs.	ARL	**< 0.0001**
	SUNA	vs.	WBL	**< 0.0001**
Spring	ARL	vs.	SUNA	**< 0.0001**
	WBL	vs.	ARL	**< 0.0001**
	SUNA	vs.	WBL	**0.0003**
Agricultural	ARL	vs.	SUNA	**< 0.0001**
	WBL	vs.	ARL	**< 0.0001**
	SUNA	vs.	WBL	0.1160
Darkwater	ARL	vs.	SUNA	**< 0.0001**
	WBL	vs.	ARL	**< 0.0001**
	SUNA	vs.	WBL	**< 0.0001**

Table 2-2. Experiment 2, comparison between 5mm SUNA, 10mm SUNA, and ARL nitrate concentration p-Values for paired method comparisons. p-Value <0.05 indicates a significant difference between the two methods being compared.

Site	Method Comparison			p-Value
	SUNA 5mm	vs.	ARL	**0.0001**
Eutrophic	SUNA 10mm	vs.	ARL	0.5362
	SUNA 5mm	vs.	SUNA 10mm	**0.004**
	SUNA 5mm	vs.	ARL	**< 0.0001**
Stormwater	SUNA 10mm	vs.	ARL	0.9471
	SUNA 5mm	vs.	SUNA 10mm	**< 0.0001**
	SUNA 5mm	vs.	ARL	**< 0.0001**
Spring	SUNA 10mm	vs.	ARL	**0.006**
	SUNA 5mm	vs.	SUNA 10mm	**0.0019**
	SUNA 5mm	vs.	ARL	**< 0.0001**
Agricultural	SUNA 10mm	vs.	ARL	**0.0032**
	SUNA 5mm	vs.	SUNA 10mm	0.0914
	SUNA 5mm	vs.	ARL	**0.0194**
Darkwater	SUNA 10mm	vs.	ARL	**< 0.0001**
	SUNA 5mm	vs.	SUNA 10mm	**< 0.0001**

Table 2-3. Comparison of known nitrate concentrations using Tukey test at an alpha level of 0.05. Letters not shared among methods indicate significant differences (α<0.05).

Site	Method				Least Sq Mean	Method				Least Sq Mean
	Experiment 1					Experiment 2				
Eutrophic	WBL	A			0.9187	SUNA 5mm	A			0.6925
	SUNA	A			0.8658	SUNA 10mm		B		0.3486
	ARL		B		0.3360	ARL		B		0.2388
Stormwater	WBL	A			0.7815	SUNA 5mm	A			0.8284
	SUNA		B		0.4164	ARL		B		0.2714
	ARL			C	0.1252	SUNA 10mm		B		0.2458
Spring	WBL	A			0.8002	SUNA 5mm	A			0.8215
	SUNA		B		0.5298	SUNA 10mm		B		0.5009
	ARL			C	0.1080	ARL			C	0.2151
Agricultural	SUNA	A			0.9405	SUNA 5mm	A			1.2770
	WBL	A			0.8032	SUNA 10mm		B		0.6709
	ARL		B		0.1670	ARL		B		0.2935
Darkwater	SUNA	A			5.8317	SUNA 10mm	A			5.8010
	WBL		B		1.4621	SUNA 5mm		B		1.0928
	ARL			C	0.0782	ARL			C	0.3201

CHAPTER 3
EFFECT OF PATH LENGTH ON OPTICAL INTERFERENCE

Introduction

The design of optical nitrate sensors including the Submersible Ultraviolet Nitrate Analyzer (SUNA) (Satlantic Inc., Halifax, NS, Canada) is based on the Beer-Lambert law of physical optics, which relates attenuation of light to the substance the light is travelling through (Satlantic, 2011). Absorbance (A), molar absorptivity of the substance (ε), and path length of the instrument (L) are used to calculate concentration (c) of the absorbing substance in solution:

$$\mathrm{c} = \frac{\mathrm{A}}{\varepsilon * \mathrm{L}} \tag{3.1}$$

The algorithm employed by the sensors uses absorption and molar absorptivity of the constituents of interest to process the raw spectral data in SUNACom software (Satlantic, 2011). However, many variables of the optical sensor come down to the path length variable in the Beer-Lambert law. The path length in an optical nitrate sensor is the distance of the optical path (where the water sample passively flows) between the light source and the detector. The path length determines accuracy, sensitivity, and detection range for the sensor (Johnson and Coletti, 2002).

An optimum path length is dependent on application. The optical path length must be short enough for adequate light to reach from the source to the detector in optically dense water. Yet the path length must also be long enough for detectable attenuation of light from the light source (incident) to the detector (transmitted) at even low concentrations of the compound of interest (Pellerin et al., 2013; Satlantic, 2011). The longer the path length, the lower the detectable range of nitrate concentrations; the shorter the path length, the greater the detectable range of nitrate concentrations. Currently, instruments used in wastewater applications, where the water has a high optical density, have short path lengths as small as 1mm. Instruments used in optically clear drinking water applications can have longer path lengths, up to 100mm (Pellerin et al., 2013).

According to theoretical considerations and experimental confirmations by Satlantic, the impact of optical interference on nitrate measurements is independent of the optical path length (2011). However, interference is not independent of absorbance as interfering species resemble the spectral characteristics of nitrate and the algorithm is unable to deconvolve the extraneous absorbance measurements. The optical path length is also related to absorbance as the SUNA only operates up to an absorbance value of 1.5 (Satlantic, 2011). This maximum absorbance measurement is reached at different levels of interference, dependent on the instrument path length (for the SUNA path lengths are fixed at either 5mm or 10mm).

In this study, the effects of path length on accuracy and sensitivity of optical nitrate sensors are compared over a range of nitrate concentrations and optical interferences. Two classes of interfering species are principal to measuring nitrate with optical sensors and are the focus of this study: suspended particulate matter or turbidity, which scatters light, and colored dissolved organic matter (CDOM), which absorbs light. To mimic natural conditions in a controlled laboratory environment, standard reference materials were selected that are reflective of natural waters in Florida. Kaolinite powder (Ward's Natural Science Establishment, Inc.) was chosen as a proxy for turbidity and

Suwannee River Natural Organic Matter (SRNOM) (International Humic Substances Society, St. Paul, MN) was chosen as a proxy for CDOM.

The objective of this study was to assess the effect of path length on optical interference when measuring nitrate with a SUNA. Accuracy and sensitivity of two SUNAs with different path lengths (5mm and 10mm) were examined over a range of nitrate concentrations (0-30 mg N L^{-1}), turbidities (0-1000 mg kaolinite L^{-1}), and CDOM concentrations (0-140 mg SRNOM L^{-1}). The motivation behind this setup was to assess the performance of the optical sensors over a range of interferences and the interaction with nitrate concentrations that can be expected at study sites.

Materials and Methods

Turbidity

Turbidity stock solutions covering a range of values to be expected in environmental systems were created in the laboratory by suspending kaolinite powder (Ward's Natural Science Establishment, 46 E 0995, Rochester, NY) in double-deionized water (18 megaohm-cm). Nine stock solutions were created with 0,10, 20, 50, 75, 100, 250, 500, and 1000 mg kaolinite L^{-1}. Stock solutions were covered and constantly stirred to maintain an even suspension of sediment.

Colored dissolved organic matter

Stock solutions covering a range of dissolved organic matter concentrations expected in environmental systems were created from Suwannee River Natural Organic Matter (SRNOM) reference material (International Humic Substances Society Catalog Number 2R101N, St. Paul, MN). Ten stock solutions were created with the following concentrations of SRNOM: 0, 0.5, 1, 2, 5, 10, 20, 40, 80, and 100 mg SR NOM L^{-1}.

Stock solutions were stored in opaque glassware to minimize photo degradation over the course of the experiment.

Nitrate spikes

To assess the accuracy of the 5mm path length and the 10mm path length SUNAs with different optical interferences present, the two interference stocks created above were spiked with a nitrate stock solution to obtain nitrate concentrations ranging from 0 mg N L^{-1} to 30 mg N L^{-1}. For every combination of optical interference (turbidity or natural organic matter) and nitrate concentration, three replicates were created and the nitrate concentration was measured optically with the two SUNA instruments. 10% of the matrix combinations were randomly selected and nitrate concentrations were validated by EPA Method 353.2 at the Analytical Research Laboratory. The experimental design is displayed in Table 3-1.

Results and Discussion

Accuracy and sensitivity of both optical nitrate sensors did not steadily decrease with increasing levels of interference, as hypothesized.

Turbidity Interference

When comparing the accuracy of a 5mm path length instrument and a 10mm path length instrument over a range of turbidity interferences, the average percent error of the nitrate measurement for both instruments was less than 10% for turbidity values up to 250 mg kaolinite L^{-1} (5mm = 9.75±0.6; 10mm = 6.50±0.9) (Table 3-2). For the 5mm path length SUNA, percent error increased to 10.26% at 500 mg kaolinite L^{-1} and 16.24% at 1000 mg kaolinite L^{-1}. These values are in line with the instrument specifications published by Satlantic who states that optical extinction can be expected at 1250 NTU for this instrument (1 mg kaolinite L^{-1} is roughly equal to 1 NTU) (Satlantic, 2011). The increased percent error at 1000 mg kaolinite L^{-1} should not be a concern to most users as those conditions only occur over short durations during peak storm flow (Saraceno et al., 2009). The 10mm path length SUNA experienced an increased percent error (28.02%) at 500 mg kaolinite L^{-1}; the manufacturer-identified limit before optical extinction occurs is 625 NTU. At 1000 mg kaolinite L^{-1}, the 10mm SUNA did experience optical extinction (100% error) (Table 3-2). Average values of variance were an order of magnitude higher for the 5mm SUNA than the 10mm SUNA for most turbidity standards in range, an occurrence not explained by the Beer-Lambert law and an area for further investigation. The average variance for both instruments increased at 250 mg kaolinite L^{-1} and 500 mg kaolinite L^{-1}, as the water became more optically dense and more particles were present to scatter incident light. It is unclear why at 1000 mg kaolinite L^{-1}, percent error for the 5mm path length SUNA increased yet the variance decreased; it is expected that this value is just an anomaly and if repeated, would follow the increasing trend (Table 3-2).

Colored dissolved organic matter interference

Interference from CDOM produced similar results to interference from turbidity. Average percent error values for CDOM were higher than turbidity, 7.53±1.03 for 10mm path length and 12.94±1.08 for 5mm path length up to 40 mg SR NOM L^{-1} (Table 3-3). At 80 mg SR NOM L^{-1} and above, the 10mm path length SUNA experienced optical extinction and no nitrate measurement was obtained (100% error). Percent error for the 5mm path length SUNA increased at 80 mg SR NOM L^{-1} to 39.4%. While optical extinction did not occur with the 5mm SUNA for the NOM concentrations tested, caution should be used with SR NOM concentrations above 80 mg SR NOM L^{-1}. Average values of variance were an order of magnitude higher for the 5mm SUNA than the 10mm SUNA for NOM standards up to 20 mg SR NOM L^{-1}, an occurrence again not explained by the Beer-Lambert law and an area for further investigation (Table 3-3). Average variance did increase for NOM standards above 20 mg SR NOM L^{-1}; natural waters with this range of concentrations warrant supplementary measurements to improve the nitrate average. Satlantic User Manual states that naturally occurring CDOM concentrations stay within the operating range of the SUNA and optical extinction will not occur (2011). However, user caution should persist with high CDOM values as optical extinction and increasing error has occurred with natural waters (Chapter 2).

Conclusions

This study illuminates some concerns of interference when using an optical nitrate analyzer in natural waters with high turbidity or CDOM. The inaccuracy of the instrument up to high levels of turbidity and CDOM (>250 mg kaolinite L^{-1} and >20 mg SR NOM L^{-1}, respectively) did present as a systemic bias, providing measurements lower than the known concentrations. These findings demonstrate the utility of optical nitrate sensors in similar conditions, provided a correction is used if absolute concentrations are needed or the instrument is used to measure relative concentrations.

Table 3-1. Experimental design of interfering constituents and nitrate spikes. Each interaction cell is referred to as a matrix cell in Appendix A. Each interaction was created and measured in triplicate with complete randomization to the order.

Kaolinite (mg/L)		0	10	20	50	75	100	250	500	1000	
SR NOM (mg/L)		0	0.5	1	2	5	10	20	40	80	100
SUNA (mm)		5 10	5 10	5 10	5 10	5 10	5 10	5 10	5 10	5 10	5 10
Nitrate as N (mg/L)	0	1	11	21	31	41	51	61	71	81	91
	0.1	2	12	22	32	42	52	62	72	82	92
	0.25	3	13	23	33	43	53	63	73	83	93
	0.5	4	14	24	34	44	54	64	74	84	94
	1	5	15	25	35	45	55	65	75	85	95
	2	6	16	26	36	46	56	66	76	86	96
	5	7	17	27	37	47	57	67	77	87	97
	10	8	18	28	38	48	58	68	78	88	98
	20	9	19	29	39	49	59	69	79	89	99
	30	10	20	30	40	50	60	70	80	90	100

Table 3-2. Summary statistics for interference from turbidity. Asterisk (*) indicates that optical extinction occurred and no nitrate value was obtained from SUNA.

Turbidity	Average Variance		Average % Error	
mg L^{-1}	5mm	10mm	5mm	10mm
0	0.30	0.06	10.01	6.74
10	0.30	0.04	9.99	6.72
20	0.43	0.02	9.10	8.06
50	0.45	0.07	9.60	5.86
75	0.48	0.04	8.91	6.14
100	0.32	0.06	10.50	6.73
250	1.72	0.55	10.10	5.25
500	2.14	0.31	10.26	28.02
1000	0.04	0.00	16.24	100.00*

Table 3-3. Summary statistics for interference from natural organic matter. Asterisk (*) indicates that optical extinction occurred and no nitrate value was obtained from SUNA.

NOM	Average Variance		Average % Error	
mg L^{-1}	5mm	10mm	5mm	10mm
0	0.23	0.02	11.79	7.82
0.5	0.30	0.03	13.86	7.45
1	0.38	0.02	12.04	8.00
2	0.47	0.02	12.25	7.83
5	0.64	0.05	12.01	6.70
10	0.80	0.03	14.39	6.46
20	0.42	0.07	14.17	6.46
40	1.39	0.50	12.09	9.55
80	3.48	0.00*	13.84	100.00*
100	3.72	0.00*	39.40	100.00*

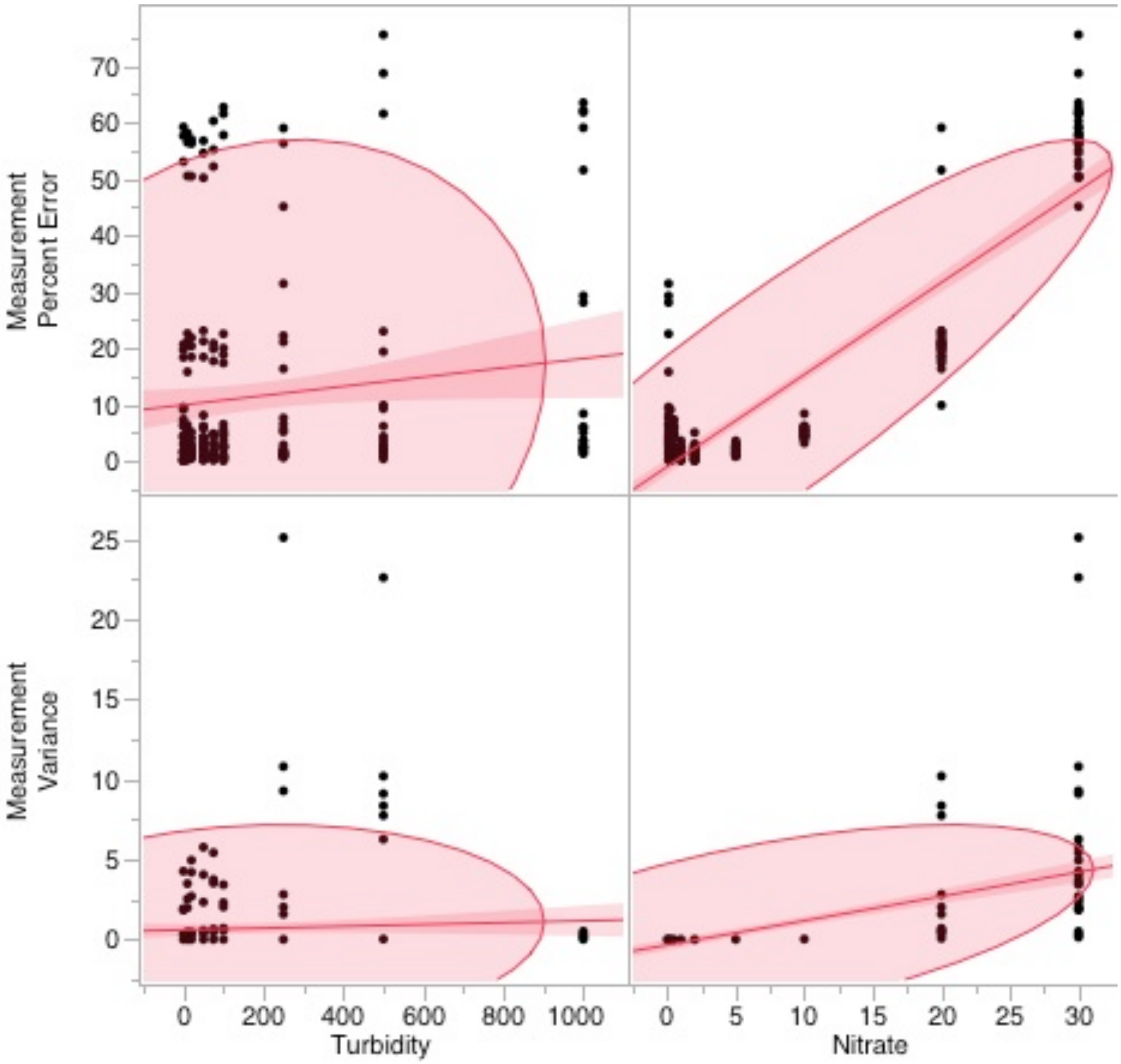

Figure 3-1. Distribution of error for 5mm path length SUNA measuring turbidity interference from suspended kaolinite.

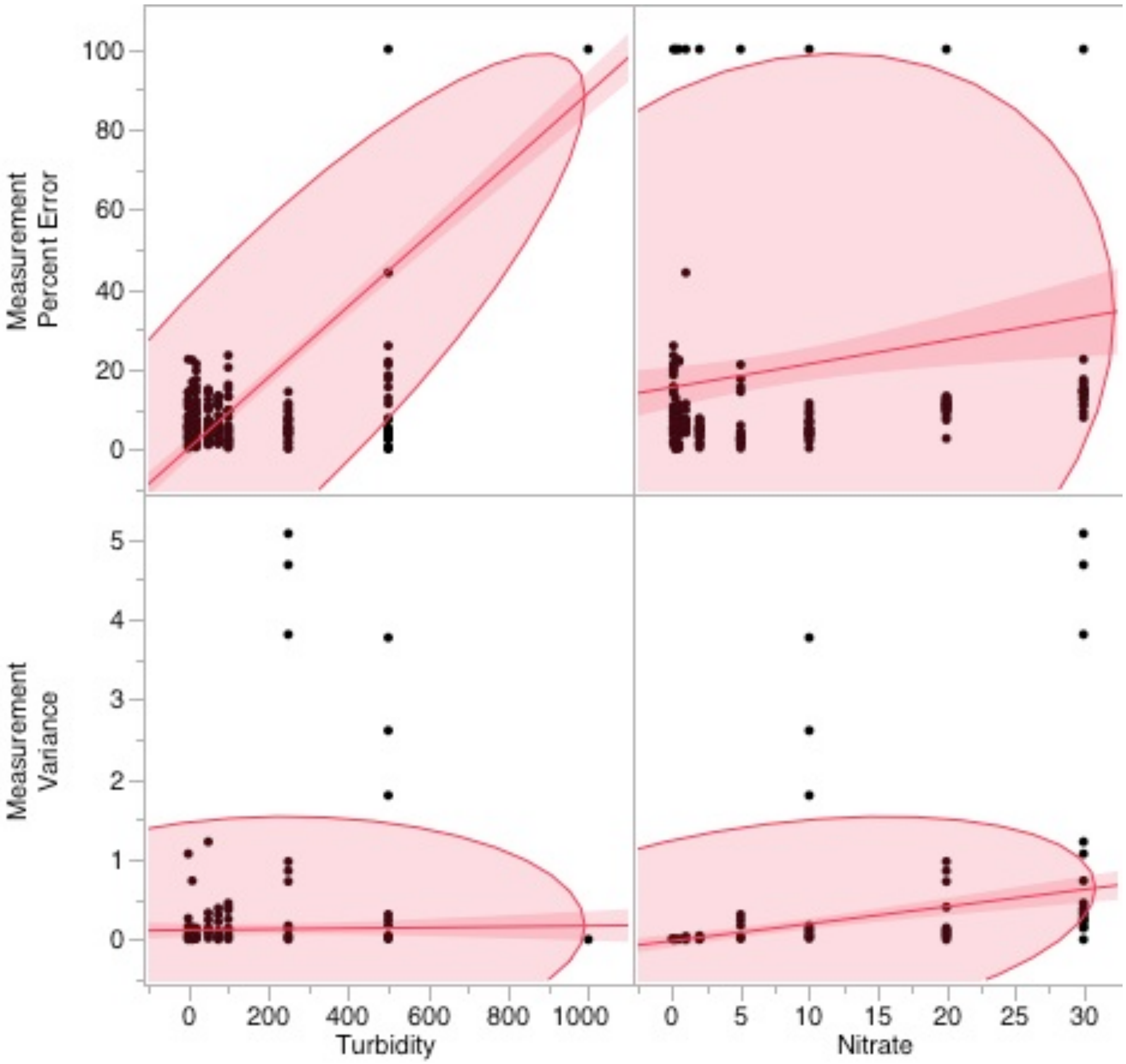

Figure 3-2. Distribution of error for 10mm path length SUNA measuring turbidity interference from suspended kaolinite.

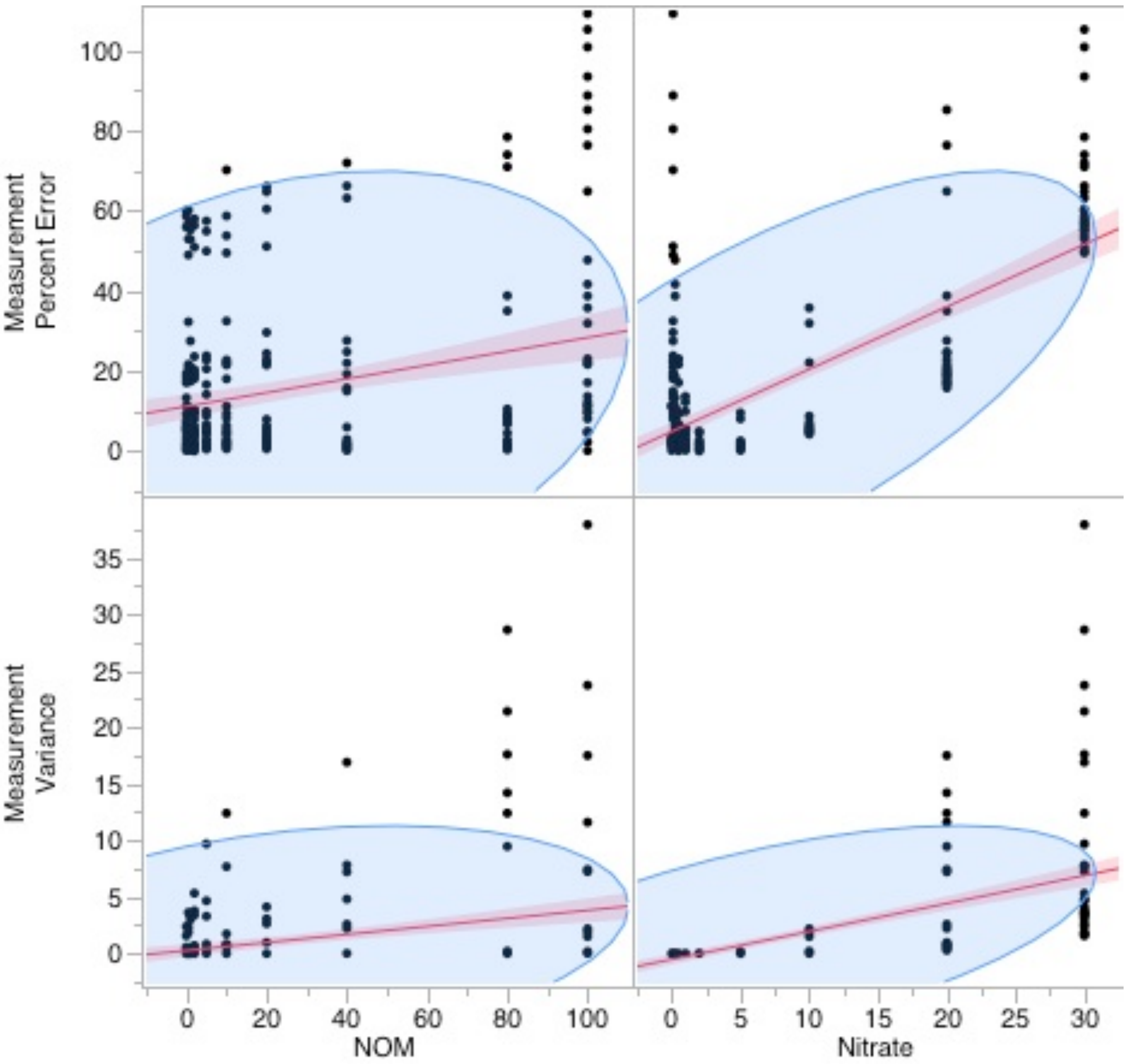

Figure 3-3. Distribution of error for 5mm path length SUNA measuring Suwannee River Natural Organic Matter interference.

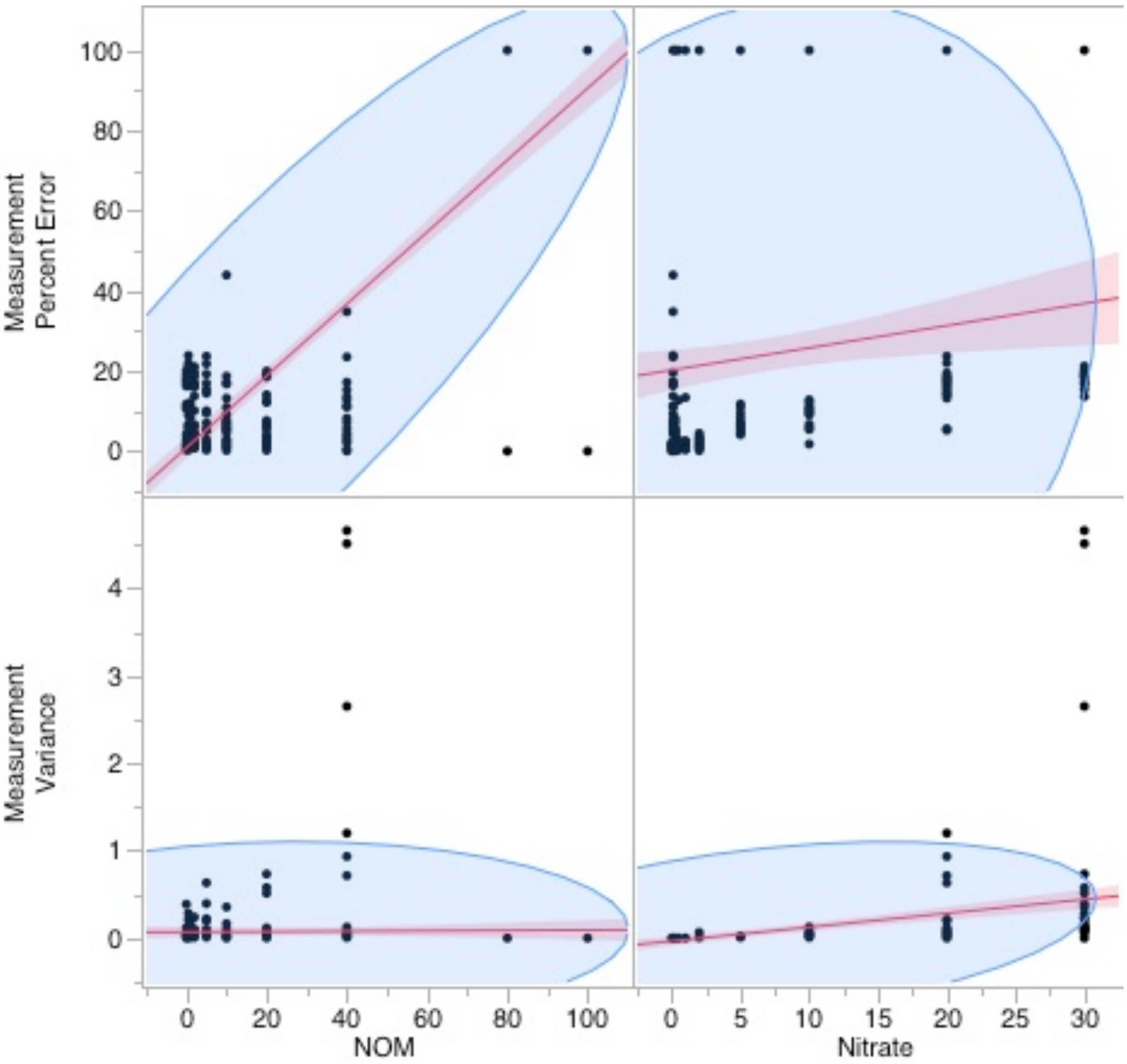

Figure 3-4. Distribution of error for 10mm path length SUNA measuring Suwannee River Natural Organic Matter interference.

CHAPTER 4
CONCLUSIONS AND RECOMMENDATIONS

Optical nitrate sensors have proven useful for providing high temporal resolution data to understand dynamic biogeochemical processes at scales difficult with traditional wet chemistry methods. This thesis has identified some differences between wet chemical and optical methods for measuring nitrate and shown that, depending on individual instrument operation and sample pretreatment, there can be a significant difference between nitrate measurements of contrasting methods on the same sample. Not only did the optical and wet chemical methods prove to be significantly different under a variety of conditions, but so did a comparison between two wet chemical methods and a comparison between two optical instruments. It is important to understand potential matrix interferences and adequately match application to instrument performance when choosing an appropriate method.

Results from Chapter 3 showed low measures of accuracy for optical nitrate sensors with two different path lengths (5mm and 10mm). The measurements of both instruments were biased lower than the known concentrations, exposing an opportunity for correction (opposed to a random error). A high level of sensitivity for the two instruments indicates the best application is as a relative measure of nitrate concentrations, not an absolute measure.

Several recommendations can be made to advance the performance of optical nitrate sensors when met with unspecified matrix effects and optical interferences including turbidity and CDOM. Sensors should be vetted thoroughly in the laboratory before deployment with the expected range of nitrate concentrations and interferences.

Testing should be completed with reference materials that are reflective of natural waters (Pellerin et al., 2013).

As in the laboratory with analytical instruments, inter-sensor differences cannot be disregarded. Sensor specific calibrations can be developed which employ extinction coefficients measured by the specific sensor as opposed to class-based calibration files, which use averaged extinction coefficients from many sensors (Satlantic, 2011).

For optically dense conditions, settings can be configured to repeat measurements with an increased spectrophotometer exposure time to extend the operating range (Satlantic, 2011). This integrative processing is built into the SUNA V2 operating system and must be manually configured in the SUNA version 1.

An in-system calibration is possible if misread voltages are causing the inaccuracy. By internally measuring the low and high voltage values generated by the sensor, offset coefficients can be calculated to correct any discrepancies (Satlantic, 2011). These corrections are not simple, but they allow the user to customize the sensor for individual needs and applications.

Overall, optical nitrate sensors offer promising advances over traditional analytical techniques. Fine adjustments can improve the accuracy to more closely equal standard laboratory methodology and with their chemical-free and real-time capabilities, optical sensors can surpass wet chemical methods on the scale of scientific questions that are possible to address.

APPENDIX A

Table A-1.

SUNA Path length (mm)	**NO_3-N** (mg L^{-1})	**Kaolinite** (mg L^{-1})	**Matrix Cell**	**Replicate**	**NO_3-N Measurement** (mg L^{-1})	**Measurement Variance**	**Measurement Difference** (mg L^{-1})	**Measurement Error** (%)
5	0	0	1	1	0.017	2.93E-06	0.017	1.68
5	0	0	1	2	0.006	3.15E-06	0.006	0.62
5	0	0	1	3	0.002	2.25E-06	0.002	0.20
10	0	0	1	1	-0.020	3.91E-06	0.020	1.99
10	0	0	1	2	-0.013	4.16E-06	0.013	1.29
10	0	0	1	3	-0.020	3.92E-06	0.020	1.96
5	0.1	0	2	1	0.090	3.52E-06	0.010	9.59
5	0.1	0	2	2	0.093	3.17E-06	0.007	6.52
5	0.1	0	2	3	0.103	3.51E-06	0.003	3.05
10	0.1	0	2	1	0.098	4.02E-06	0.002	1.59
10	0.1	0	2	2	0.092	4.51E-06	0.008	8.07
10	0.1	0	2	3	0.096	4.21E-06	0.004	3.91
5	0.25	0	3	1	0.250	3.70E-06	0.000	0.08
5	0.25	0	3	2	0.254	3.06E-06	0.004	1.75
5	0.25	0	3	3	0.273	4.53E-06	0.023	9.14
10	0.25	0	3	1	0.249	4.10E-06	0.001	0.45
10	0.25	0	3	2	0.252	4.19E-06	0.002	0.98
10	0.25	0	3	3	0.258	4.84E-06	0.008	3.32
5	0.5	0	4	1	0.522	2.77E-06	0.022	4.37
5	0.5	0	4	2	0.537	4.08E-06	0.037	7.37
5	0.5	0	4	3	0.531	4.91E-06	0.031	6.23
10	0.5	0	4	1	0.539	6.21E-06	0.039	7.79
10	0.5	0	4	2	0.556	8.36E-06	0.056	11.17
10	0.5	0	4	3	0.542	4.94E-06	0.042	8.45
5	1	0	5	1	1.004	2.80E-06	0.004	0.42
5	1	0	5	2	1.002	4.50E-06	0.002	0.16
5	1	0	5	3	1.005	5.21E-06	0.005	0.45
10	1	0	5	1	1.044	1.20E-05	0.044	4.44
10	1	0	5	2	1.055	9.32E-06	0.055	5.54
10	1	0	5	3	1.061	1.31E-05	0.061	6.13
5	2	0	6	1	1.973	5.98E-06	0.027	1.34

5	2	0	6	2	1.994	5.24E-06	0.006	0.30
5	2	0	6	3	2.001	5.82E-06	0.001	0.07
10	2	0	6	1	2.098	4.63E-05	0.098	4.90
10	2	0	6	2	2.114	3.82E-05	0.114	5.68
10	2	0	6	3	2.120	4.10E-05	0.120	6.00
5	5	0	7	1	4.921	3.20E-05	0.079	1.57
5	5	0	7	2	4.905	6.00E-05	0.095	1.91
5	5	0	7	3	4.909	3.52E-04	0.091	1.82
10	5	0	7	1	5.153	2.18E-03	0.153	3.06
10	5	0	7	2	5.123	3.09E-03	0.123	2.46
10	5	0	7	3	5.143	1.73E-03	0.143	2.86
5	10	0	8	1	9.542	8.18E-04	0.458	4.58
5	10	0	8	2	9.551	1.27E-03	0.449	4.49
5	10	0	8	3	9.586	1.35E-03	0.414	4.14
10	10	0	8	1	9.319	1.76E-02	0.681	6.81
10	10	0	8	2	8.953	2.15E-02	1.047	10.47
10	10	0	8	3	9.464	1.61E-02	0.536	5.36
5	20	0	9	1	15.866	3.34E-01	4.134	20.67
5	20	0	9	2	16.056	3.01E-01	3.944	19.72
5	20	0	9	3	16.325	2.99E-01	3.675	18.38
10	20	0	9	1	17.474	3.64E-02	2.526	12.63
10	20	0	9	2	17.683	1.15E-01	2.317	11.59
10	20	0	9	3	17.543	6.47E-02	2.457	12.29
5	30	0	10	1	12.719	1.84E+00	17.281	57.60
5	30	0	10	2	12.255	1.92E+00	17.745	59.15
5	30	0	10	3	14.095	4.26E+00	15.905	53.02
10	30	0	10	1	25.684	1.07E+00	4.316	14.39
10	30	0	10	2	23.243	2.63E-01	6.757	22.52
10	30	0	10	3	25.735	1.62E-01	4.265	14.22
5	0	10	11	1	0.006	3.29E-06	0.006	0.63
5	0	10	11	2	0.014	2.87E-06	0.014	1.42
5	0	10	11	3	0.051	3.81E-06	0.051	5.13
10	0	10	11	1	-0.017	4.76E-06	0.017	1.73
10	0	10	11	2	-0.018	3.89E-06	0.018	1.82
10	0	10	11	3	0.023	1.44E-05	0.023	2.26
5	0.1	10	12	1	0.106	4.18E-06	0.006	6.40
5	0.1	10	12	2	0.106	2.81E-06	0.006	5.65
5	0.1	10	12	3	0.116	4.83E-06	0.016	15.82
10	0.1	10	12	1	0.090	3.74E-06	0.010	10.01
10	0.1	10	12	2	0.085	4.72E-06	0.015	15.28
10	0.1	10	12	3	0.098	3.98E-06	0.002	1.96
5	0.25	10	13	1	0.252	2.69E-06	0.002	0.97
5	0.25	10	13	2	0.251	3.69E-06	0.001	0.36
5	0.25	10	13	3	0.253	4.26E-06	0.003	1.09
10	0.25	10	13	1	0.259	4.46E-06	0.009	3.58
10	0.25	10	13	2	0.254	4.29E-06	0.004	1.44

10	0.25	10	13	3	0.260	5.94E-06	0.010	3.99
5	0.5	10	14	1	0.497	3.10E-06	0.003	0.52
5	0.5	10	14	2	0.494	4.70E-06	0.006	1.21
5	0.5	10	14	3	0.478	5.22E-06	0.022	4.37
10	0.5	10	14	1	0.530	1.19E-05	0.030	6.02
10	0.5	10	14	2	0.531	1.02E-05	0.031	6.16
10	0.5	10	14	3	0.612	8.44E-06	0.112	22.36
5	1	10	15	1	0.992	3.70E-06	0.008	0.81
5	1	10	15	2	1.003	6.74E-06	0.003	0.25
5	1	10	15	3	1.003	3.96E-06	0.003	0.34
10	1	10	15	1	1.047	1.49E-05	0.047	4.66
10	1	10	15	2	1.052	1.18E-05	0.052	5.25
10	1	10	15	3	1.054	1.26E-05	0.054	5.37
5	2	10	16	1	1.967	9.25E-06	0.033	1.66
5	2	10	16	2	1.970	8.63E-06	0.030	1.49
5	2	10	16	3	1.978	7.71E-06	0.022	1.09
10	2	10	16	1	2.073	9.29E-05	0.073	3.67
10	2	10	16	2	2.073	1.59E-04	0.073	3.67
10	2	10	16	3	2.099	2.86E-05	0.099	4.96
5	5	10	17	1	4.842	3.11E-05	0.158	3.16
5	5	10	17	2	4.944	4.31E-05	0.056	1.13
5	5	10	17	3	4.922	3.83E-05	0.078	1.57
10	5	10	17	1	5.050	2.99E-03	0.050	1.01
10	5	10	17	2	5.142	1.49E-03	0.142	2.84
10	5	10	17	3	5.167	9.37E-04	0.167	3.33
5	10	10	18	1	9.474	1.48E-03	0.526	5.26
5	10	10	18	2	9.498	1.31E-03	0.502	5.02
5	10	10	18	3	9.503	1.04E-03	0.497	4.97
10	10	10	18	1	9.442	1.74E-02	0.558	5.58
10	10	10	18	2	9.502	1.50E-02	0.498	4.98
10	10	10	18	3	9.580	1.15E-02	0.420	4.20
5	20	10	19	1	15.754	4.65E-01	4.246	21.23
5	20	10	19	2	15.476	3.27E-01	4.524	22.62
5	20	10	19	3	15.886	2.96E-01	4.114	20.57
10	20	10	19	1	17.830	1.18E-01	2.170	10.85
10	20	10	19	2	18.063	6.45E-02	1.937	9.68
10	20	10	19	3	18.199	4.72E-02	1.801	9.01
5	30	10	20	1	13.072	2.53E+00	16.928	56.43
5	30	10	20	2	12.580	1.98E+00	17.420	58.07
5	30	10	20	3	14.854	3.49E+00	15.146	50.49
10	30	10	20	1	24.936	1.53E-01	5.064	16.88
10	30	10	20	2	25.558	7.33E-01	4.442	14.81
10	30	10	20	3	25.724	1.53E-01	4.276	14.25
5	0	20	21	1	0.009	3.35E-06	0.009	0.90
5	0	20	21	2	0.010	4.30E-06	0.010	1.00
5	0	20	21	3	0.014	4.52E-06	0.014	1.42

10	0	20	21	1	-0.020	4.38E-06	0.020	1.97
10	0	20	21	2	-0.018	4.60E-06	0.018	1.80
10	0	20	21	3	-0.015	5.28E-06	0.015	1.49
5	0.1	20	22	1	0.097	3.66E-06	0.003	2.74
5	0.1	20	22	2	0.096	3.37E-06	0.004	4.05
5	0.1	20	22	3	0.102	3.73E-06	0.002	2.20
10	0.1	20	22	1	0.084	6.03E-06	0.016	15.72
10	0.1	20	22	2	0.079	5.51E-06	0.021	21.37
10	0.1	20	22	3	0.080	5.60E-06	0.020	19.73
5	0.25	20	23	1	0.247	5.28E-06	0.003	1.04
5	0.25	20	23	2	0.248	4.30E-06	0.002	0.72
5	0.25	20	23	3	0.251	3.31E-06	0.001	0.51
10	0.25	20	23	1	0.251	7.99E-06	0.001	0.59
10	0.25	20	23	2	0.252	6.76E-06	0.002	0.71
10	0.25	20	23	3	0.253	4.94E-06	0.003	1.29
5	0.5	20	24	1	0.507	4.30E-06	0.007	1.46
5	0.5	20	24	2	0.503	3.20E-06	0.003	0.51
5	0.5	20	24	3	0.507	5.03E-06	0.007	1.32
10	0.5	20	24	1	0.534	5.53E-06	0.034	6.79
10	0.5	20	24	2	0.528	6.72E-06	0.028	5.61
10	0.5	20	24	3	0.530	6.18E-06	0.030	5.91
5	1	20	25	1	1.017	5.28E-06	0.017	1.65
5	1	20	25	2	1.029	4.50E-06	0.029	2.89
5	1	20	25	3	1.020	5.83E-06	0.020	1.95
10	1	20	25	1	1.054	1.14E-05	0.054	5.38
10	1	20	25	2	1.071	1.63E-05	0.071	7.13
10	1	20	25	3	1.075	1.63E-05	0.075	7.54
5	2	20	26	1	1.977	5.97E-06	0.023	1.14
5	2	20	26	2	1.960	8.10E-06	0.040	1.98
5	2	20	26	3	1.970	7.56E-06	0.030	1.51
10	2	20	26	1	2.098	3.39E-05	0.098	4.91
10	2	20	26	2	2.144	7.38E-05	0.144	7.19
10	2	20	26	3	2.110	1.05E-04	0.110	5.48
5	5	20	27	1	4.902	3.84E-05	0.098	1.95
5	5	20	27	2	4.942	3.25E-05	0.058	1.16
5	5	20	27	3	4.958	3.27E-05	0.042	0.85
10	5	20	27	1	4.697	4.21E-03	0.303	6.06
10	5	20	27	2	4.795	3.67E-03	0.205	4.09
10	5	20	27	3	5.108	1.36E-03	0.108	2.16
5	10	20	28	1	9.483	1.26E-03	0.517	5.17
5	10	20	28	2	9.471	1.23E-03	0.529	5.29
5	10	20	28	3	9.463	1.52E-03	0.537	5.37
10	10	20	28	1	9.102	5.28E-03	0.898	8.98
10	10	20	28	2	9.059	8.60E-03	0.941	9.41
10	10	20	28	3	9.318	2.92E-02	0.682	6.82
5	20	20	29	1	15.630	2.71E-01	4.370	21.85

5	20	20	29	2	15.922	4.29E-01	4.078	20.39
5	20	20	29	3	16.309	4.47E-01	3.691	18.46
10	20	20	29	1	17.740	4.55E-02	2.260	11.30
10	20	20	29	2	17.535	1.20E-01	2.465	12.33
10	20	20	29	3	17.949	4.91E-02	2.051	10.26
5	30	20	30	1	12.915	2.70E+00	17.085	56.95
5	30	20	30	2	13.135	4.95E+00	16.865	56.22
5	30	20	30	3	14.872	4.20E+00	15.128	50.43
10	30	20	30	1	24.740	1.33E-01	5.260	17.53
10	30	20	30	2	24.689	1.36E-01	5.311	17.70
10	30	20	30	3	25.670	1.42E-01	4.330	14.43
5	0	50	31	1	-0.001	5.22E-06	0.001	0.14
5	0	50	31	2	-0.004	4.20E-06	0.004	0.37
5	0	50	31	3	0.001	4.31E-06	0.001	0.07
10	0	50	31	1	-0.019	8.62E-06	0.019	1.87
10	0	50	31	2	-0.018	7.24E-06	0.018	1.79
10	0	50	31	3	-0.016	6.53E-06	0.016	1.60
5	0.1	50	32	1	0.108	3.15E-06	0.008	8.15
5	0.1	50	32	2	0.104	4.63E-06	0.004	4.24
5	0.1	50	32	3	0.103	4.23E-06	0.003	3.36
10	0.1	50	32	1	0.096	6.94E-06	0.004	3.72
10	0.1	50	32	2	0.093	7.96E-06	0.007	7.04
10	0.1	50	32	3	0.086	1.13E-04	0.014	14.13
5	0.25	50	33	1	0.244	5.11E-06	0.006	2.41
5	0.25	50	33	2	0.246	5.73E-06	0.004	1.48
5	0.25	50	33	3	0.244	3.26E-06	0.006	2.21
10	0.25	50	33	1	0.245	1.11E-05	0.005	1.88
10	0.25	50	33	2	0.256	2.99E-05	0.006	2.36
10	0.25	50	33	3	0.255	1.01E-05	0.005	2.02
5	0.5	50	34	1	0.513	4.24E-06	0.013	2.58
5	0.5	50	34	2	0.512	5.51E-06	0.012	2.47
5	0.5	50	34	3	0.530	8.37E-06	0.030	5.97
10	0.5	50	34	1	0.535	2.62E-05	0.035	7.01
10	0.5	50	34	2	0.525	1.39E-05	0.025	4.91
10	0.5	50	34	3	0.537	1.36E-05	0.037	7.46
5	1	50	35	1	0.991	4.95E-06	0.009	0.88
5	1	50	35	2	0.980	5.02E-06	0.020	2.03
5	1	50	35	3	1.009	5.84E-05	0.009	0.94
10	1	50	35	1	1.049	3.08E-05	0.049	4.95
10	1	50	35	2	1.042	1.86E-05	0.042	4.17
10	1	50	35	3	1.066	1.41E-05	0.066	6.61
5	2	50	36	1	2.004	6.47E-06	0.004	0.20
5	2	50	36	2	1.988	1.05E-05	0.012	0.62
5	2	50	36	3	2.005	9.72E-06	0.005	0.26
10	2	50	36	1	2.123	9.89E-05	0.123	6.16
10	2	50	36	2	2.063	7.32E-05	0.063	3.17

10	2	50	36	3	2.025	9.26E-05	0.025	1.24
5	5	50	37	1	4.882	4.05E-05	0.118	2.35
5	5	50	37	2	4.819	4.18E-05	0.181	3.63
5	5	50	37	3	4.857	3.64E-05	0.143	2.85
10	5	50	37	1	5.110	1.65E-03	0.110	2.19
10	5	50	37	2	5.064	1.35E-03	0.064	1.28
10	5	50	37	3	5.100	2.40E-03	0.100	2.01
5	10	50	38	1	9.377	1.33E-03	0.624	6.24
5	10	50	38	2	9.568	1.94E-03	0.432	4.32
5	10	50	38	3	9.410	1.54E-03	0.591	5.91
10	10	50	38	1	9.639	1.39E-02	0.361	3.61
10	10	50	38	2	9.580	1.49E-02	0.420	4.20
10	10	50	38	3	9.311	7.32E-02	0.689	6.89
5	20	50	39	1	16.312	5.60E-01	3.688	18.44
5	20	50	39	2	15.751	3.98E-01	4.249	21.25
5	20	50	39	3	15.382	3.43E-01	4.618	23.09
10	20	50	39	1	17.791	1.46E-01	2.209	11.04
10	20	50	39	2	17.893	1.10E-01	2.107	10.53
10	20	50	39	3	18.033	7.51E-02	1.967	9.84
5	30	50	40	1	12.987	2.33E+00	17.013	56.71
5	30	50	40	2	13.637	4.05E+00	16.363	54.54
5	30	50	40	3	14.948	5.76E+00	15.052	50.17
10	30	50	40	1	25.481	2.46E-01	4.519	15.06
10	30	50	40	2	26.254	1.22E+00	3.746	12.49
10	30	50	40	3	25.603	3.32E-01	4.397	14.66
5	0	75	41	1	0.012	4.91E-06	0.012	1.16
5	0	75	41	2	0.005	5.92E-06	0.005	0.46
5	0	75	41	3	0.000	4.49E-06	0.000	0.04
10	0	75	41	1	-0.014	1.05E-05	0.014	1.36
10	0	75	41	2	-0.025	1.28E-05	0.025	2.52
10	0	75	41	3	-0.025	1.08E-05	0.025	2.54
5	0.1	75	42	1	0.100	6.05E-06	0.000	0.24
5	0.1	75	42	2	0.095	4.90E-06	0.005	4.88
5	0.1	75	42	3	0.096	4.58E-06	0.004	4.43
10	0.1	75	42	1	0.094	1.20E-05	0.006	5.51
10	0.1	75	42	2	0.091	2.57E-05	0.009	8.55
10	0.1	75	42	3	0.089	1.33E-05	0.011	10.85
5	0.25	75	43	1	0.254	7.18E-06	0.004	1.54
5	0.25	75	43	2	0.252	6.16E-06	0.002	0.76
5	0.25	75	43	3	0.252	5.99E-06	0.002	0.97
10	0.25	75	43	1	0.254	2.17E-05	0.004	1.59
10	0.25	75	43	2	0.256	2.39E-05	0.006	2.28
10	0.25	75	43	3	0.254	1.40E-05	0.004	1.72
5	0.5	75	44	1	0.506	8.05E-06	0.006	1.17
5	0.5	75	44	2	0.503	5.62E-06	0.003	0.57
5	0.5	75	44	3	0.495	4.62E-06	0.005	0.91

10	0.5	75	44	1	0.534	2.36E-05	0.034	6.72
10	0.5	75	44	2	0.534	2.19E-05	0.034	6.86
10	0.5	75	44	3	0.528	1.64E-05	0.028	5.68
5	1	75	45	1	0.993	6.97E-06	0.007	0.72
5	1	75	45	2	1.002	5.32E-06	0.002	0.25
5	1	75	45	3	0.994	5.03E-06	0.006	0.63
10	1	75	45	1	1.067	3.04E-05	0.067	6.75
10	1	75	45	2	1.068	2.46E-05	0.068	6.84
10	1	75	45	3	1.056	2.22E-05	0.056	5.57
5	2	75	46	1	1.939	1.05E-05	0.061	3.07
5	2	75	46	2	1.957	1.12E-05	0.043	2.16
5	2	75	46	3	1.982	8.85E-06	0.018	0.89
10	2	75	46	1	2.075	1.89E-04	0.075	3.76
10	2	75	46	2	2.096	1.52E-04	0.096	4.78
10	2	75	46	3	2.105	1.37E-04	0.105	5.25
5	5	75	47	1	4.933	9.20E-05	0.067	1.34
5	5	75	47	2	4.946	8.89E-05	0.054	1.08
5	5	75	47	3	4.943	7.73E-05	0.057	1.15
10	5	75	47	1	4.923	3.56E-02	0.077	1.54
10	5	75	47	2	4.777	1.72E-03	0.223	4.46
10	5	75	47	3	4.837	8.46E-03	0.163	3.26
5	10	75	48	1	9.523	1.92E-03	0.477	4.77
5	10	75	48	2	9.512	1.72E-03	0.488	4.88
5	10	75	48	3	9.677	2.52E-03	0.323	3.23
10	10	75	48	1	9.618	9.76E-03	0.382	3.82
10	10	75	48	2	9.638	1.52E-02	0.362	3.62
10	10	75	48	3	9.484	2.00E-02	0.516	5.16
5	20	75	49	1	16.452	4.72E-01	3.548	17.74
5	20	75	49	2	16.024	6.41E-01	3.976	19.88
5	20	75	49	3	15.826	5.90E-01	4.174	20.87
10	20	75	49	1	17.678	9.85E-02	2.322	11.61
10	20	75	49	2	17.364	5.14E-02	2.636	13.18
10	20	75	49	3	17.761	1.05E-01	2.239	11.19
5	30	75	50	1	14.352	5.42E+00	15.648	52.16
5	30	75	50	2	13.454	3.52E+00	16.546	55.15
5	30	75	50	3	11.935	3.74E+00	18.065	60.22
10	30	75	50	1	26.262	2.22E-01	3.738	12.46
10	30	75	50	2	26.643	3.89E-01	3.357	11.19
10	30	75	50	3	25.952	3.09E-01	4.048	13.49
5	0	100	51	1	0.005	5.84E-06	0.005	0.55
5	0	100	51	2	0.005	7.28E-06	0.005	0.52
5	0	100	51	3	0.004	6.53E-06	0.004	0.39
10	0	100	51	1	-0.021	1.14E-05	0.021	2.13
10	0	100	51	2	-0.022	7.24E-06	0.022	2.24
10	0	100	51	3	-0.023	1.19E-05	0.023	2.34
5	0.1	100	52	1	0.123	4.25E-06	0.023	22.55

5	0.1	100	52	2	0.104	4.95E-06	0.004	3.70
5	0.1	100	52	3	0.100	6.76E-06	0.000	0.39
10	0.1	100	52	1	0.110	1.25E-05	0.010	9.70
10	0.1	100	52	2	0.080	2.35E-05	0.020	20.49
10	0.1	100	52	3	0.076	1.42E-05	0.024	23.53
5	0.25	100	53	1	0.266	3.98E-06	0.016	6.55
5	0.25	100	53	2	0.257	8.65E-06	0.007	2.90
5	0.25	100	53	3	0.250	6.81E-06	0.000	0.07
10	0.25	100	53	1	0.260	2.93E-05	0.010	3.94
10	0.25	100	53	2	0.252	2.83E-05	0.002	0.68
10	0.25	100	53	3	0.247	2.01E-05	0.003	1.21
5	0.5	100	54	1	0.504	6.21E-06	0.004	0.80
5	0.5	100	54	2	0.503	5.87E-06	0.003	0.53
5	0.5	100	54	3	0.507	7.74E-06	0.007	1.33
10	0.5	100	54	1	0.530	2.48E-05	0.030	6.00
10	0.5	100	54	2	0.548	2.74E-05	0.048	9.59
10	0.5	100	54	3	0.528	1.89E-05	0.028	5.52
5	1	100	55	1	1.023	8.82E-06	0.023	2.29
5	1	100	55	2	1.010	5.64E-06	0.010	1.03
5	1	100	55	3	1.006	6.20E-06	0.006	0.56
10	1	100	55	1	1.099	3.33E-05	0.099	9.85
10	1	100	55	2	1.047	4.82E-05	0.047	4.70
10	1	100	55	3	1.052	9.23E-05	0.052	5.20
5	2	100	56	1	1.950	9.36E-06	0.050	2.48
5	2	100	56	2	1.898	9.59E-06	0.102	5.09
5	2	100	56	3	1.950	1.03E-05	0.050	2.48
10	2	100	56	1	2.024	1.89E-04	0.024	1.22
10	2	100	56	2	2.037	1.26E-04	0.037	1.85
10	2	100	56	3	2.009	1.66E-04	0.009	0.47
5	5	100	57	1	4.872	4.97E-05	0.128	2.57
5	5	100	57	2	4.854	4.78E-03	0.146	2.91
5	5	100	57	3	4.877	6.54E-05	0.123	2.47
10	5	100	57	1	5.116	1.35E-03	0.116	2.32
10	5	100	57	2	5.148	2.09E-03	0.148	2.96
10	5	100	57	3	5.121	5.50E-03	0.121	2.42
5	10	100	58	1	9.521	2.90E-03	0.479	4.79
5	10	100	58	2	9.557	2.48E-03	0.443	4.43
5	10	100	58	3	9.438	2.59E-03	0.562	5.62
10	10	100	58	1	9.689	1.08E-02	0.311	3.11
10	10	100	58	2	9.563	2.23E-02	0.437	4.37
10	10	100	58	3	9.797	1.13E-01	0.203	2.03
5	20	100	59	1	16.525	6.91E-01	3.475	17.38
5	20	100	59	2	16.230	5.78E-01	3.770	18.85
5	20	100	59	3	15.995	5.49E-01	4.005	20.02
10	20	100	59	1	18.390	5.58E-02	1.610	8.05
10	20	100	59	2	18.347	1.38E-01	1.653	8.26

10	20	100	59	3	17.343	4.04E-01	2.657	13.29
5	30	100	60	1	12.681	3.42E+00	17.319	57.73
5	30	100	60	2	11.203	2.03E+00	18.797	62.66
5	30	100	60	3	11.553	2.30E+00	18.447	61.49
10	30	100	60	1	25.154	4.53E-01	4.846	16.15
10	30	100	60	2	26.040	2.54E-01	3.960	13.20
10	30	100	60	3	25.458	3.69E-01	4.542	15.14
5	0	250	61	1	-0.002	1.19E-05	0.002	0.17
5	0	250	61	2	-0.003	1.75E-05	0.003	0.33
5	0	250	61	3	-0.001	1.35E-05	0.001	0.11
10	0	250	61	1	-0.015	1.31E-04	0.015	1.47
10	0	250	61	2	-0.010	1.34E-04	0.010	1.00
10	0	250	61	3	-0.013	8.74E-05	0.013	1.31
5	0.1	250	62	1	0.131	1.98E-05	0.031	31.44
5	0.1	250	62	2	0.108	1.52E-05	0.008	7.66
5	0.1	250	62	3	0.107	1.08E-05	0.007	6.58
10	0.1	250	62	1	0.105	7.98E-05	0.005	5.23
10	0.1	250	62	2	0.095	8.27E-05	0.005	4.53
10	0.1	250	62	3	0.094	7.85E-05	0.006	5.78
5	0.25	250	63	1	0.253	1.49E-05	0.003	1.31
5	0.25	250	63	2	0.252	1.43E-05	0.002	0.81
5	0.25	250	63	3	0.248	1.61E-05	0.002	0.70
10	0.25	250	63	1	0.255	1.05E-04	0.005	1.86
10	0.25	250	63	2	0.240	1.14E-04	0.010	4.05
10	0.25	250	63	3	0.263	2.52E-04	0.013	5.22
5	0.5	250	64	1	0.494	1.10E-05	0.006	1.15
5	0.5	250	64	2	0.497	1.00E-05	0.003	0.69
5	0.5	250	64	3	0.492	1.19E-05	0.008	1.56
10	0.5	250	64	1	0.507	9.60E-05	0.007	1.49
10	0.5	250	64	2	0.499	7.22E-05	0.001	0.29
10	0.5	250	64	3	0.520	9.73E-05	0.020	4.06
5	1	250	65	1	0.992	1.39E-05	0.008	0.84
5	1	250	65	2	0.988	1.71E-05	0.012	1.15
5	1	250	65	3	0.985	1.17E-05	0.015	1.54
10	1	250	65	1	1.065	1.23E-04	0.065	6.55
10	1	250	65	2	1.065	2.72E-04	0.065	6.50
10	1	250	65	3	1.055	2.06E-04	0.055	5.52
5	2	250	66	1	1.942	3.15E-05	0.058	2.90
5	2	250	66	2	1.961	2.76E-05	0.039	1.97
5	2	250	66	3	1.975	2.81E-05	0.025	1.24
10	2	250	66	1	2.077	9.97E-04	0.077	3.85
10	2	250	66	2	2.146	1.21E-03	0.146	7.32
10	2	250	66	3	2.099	1.95E-03	0.099	4.97
5	5	250	67	1	4.895	1.07E-04	0.105	2.10
5	5	250	67	2	4.954	1.87E-04	0.046	0.92
5	5	250	67	3	4.920	1.31E-04	0.080	1.59

10	5	250	67	1	4.983	8.38E-03	0.017	0.33
10	5	250	67	2	5.006	2.30E-02	0.006	0.12
10	5	250	67	3	4.278	3.53E-02	0.722	14.43
5	10	250	68	1	9.479	5.57E-03	0.521	5.21
5	10	250	68	2	9.434	4.43E-03	0.566	5.66
5	10	250	68	3	9.455	4.14E-03	0.545	5.45
10	10	250	68	1	9.615	4.45E-02	0.385	3.85
10	10	250	68	2	9.226	1.72E-01	0.774	7.74
10	10	250	68	3	8.844	1.28E-01	1.156	11.56
5	20	250	69	1	16.726	2.81E+00	3.274	16.37
5	20	250	69	2	15.777	2.02E+00	4.223	21.12
5	20	250	69	3	15.555	1.58E+00	4.445	22.22
10	20	250	69	1	18.529	7.25E-01	1.471	7.36
10	20	250	69	2	18.004	8.57E-01	1.996	9.98
10	20	250	69	3	19.447	9.73E-01	0.553	2.76
5	30	250	70	1	16.476	2.51E+01	13.524	45.08
5	30	250	70	2	13.115	1.08E+01	16.885	56.28
5	30	250	70	3	12.315	9.28E+00	17.685	58.95
10	30	250	70	1	27.186	3.81E+00	2.814	9.38
10	30	250	70	2	26.707	4.68E+00	3.293	10.98
10	30	250	70	3	27.595	5.07E+00	2.405	8.02
5	0	500	71	1	0.003	8.94E-05	0.003	0.25
5	0	500	71	2	0.003	5.89E-05	0.003	0.30
5	0	500	71	3	0.003	7.79E-05	0.003	0.29
10	0	500	71	1	-0.017	1.19E-03	0.017	1.69
10	0	500	71	2	-0.012	3.00E-03	0.012	1.23
10	0	500	71	3	-0.052	6.81E-03	0.052	5.18
5	0.1	500	72	1	0.091	3.01E-05	0.009	9.31
5	0.1	500	72	2	0.101	4.55E-05	0.001	1.09
5	0.1	500	72	3	0.098	4.63E-05	0.002	1.61
10	0.1	500	72	1	0.074	6.69E-04	0.026	25.92
10	0.1	500	72	2	0.095	1.07E-03	0.005	4.99
10	0.1	500	72	3	0.081	9.56E-04	0.019	18.61
5	0.25	500	73	1	0.247	5.41E-05	0.003	1.35
5	0.25	500	73	2	0.243	6.78E-05	0.007	2.98
5	0.25	500	73	3	0.243	6.28E-05	0.007	2.69
10	0.25	500	73	1	0.242	1.30E-03	0.008	3.06
10	0.25	500	73	2	0.250	2.81E-03	0.000	0.14
10	0.25	500	73	3	0.218	2.56E-03	0.032	12.86
5	0.5	500	74	1	0.507	6.06E-05	0.007	1.42
5	0.5	500	74	2	0.511	5.55E-05	0.011	2.19
5	0.5	500	74	3	0.509	4.95E-05	0.009	1.71
10	0.5	500	74	1	0.482	2.60E-03	0.018	3.51
10	0.5	500	74	2	0.496	6.48E-03	0.004	0.70
10	0.5	500	74	3	0.390	4.76E-03	0.110	21.94
5	1	500	75	1	1.004	5.36E-05	0.004	0.43

5	1	500	75	2	0.995	9.37E-05	0.005	0.46
5	1	500	75	3	1.002	7.43E-05	0.002	0.22
10	1	500	75	1	0.926	2.68E-02	0.074	7.41
10	1	500	75	2	0.886	3.81E-02	0.114	11.44
10	1	500	75	3	0.558	3.80E-02	0.442	44.18
5	2	500	76	1	1.990	6.21E-05	0.010	0.48
5	2	500	76	2	1.977	7.40E-05	0.023	1.14
5	2	500	76	3	1.969	9.17E-05	0.031	1.54
10	2	500	76	1	1.844	2.26E-02	0.156	7.82
10	2	500	76	2	2.060	4.66E-02	0.060	2.99
10	2	500	76	3	1.913	4.52E-02	0.087	4.36
5	5	500	77	1	4.913	5.14E-04	0.087	1.74
5	5	500	77	2	4.919	5.52E-04	0.081	1.61
5	5	500	77	3	4.871	4.47E-04	0.129	2.57
10	5	500	77	1	3.940	1.75E-01	1.060	21.19
10	5	500	77	2	4.120	2.46E-01	0.880	17.60
10	5	500	77	3	4.220	3.12E-01	0.780	15.59
5	10	500	78	1	9.615	2.45E-02	0.385	3.85
5	10	500	78	2	9.562	2.24E-02	0.438	4.38
5	10	500	78	3	9.380	1.80E-02	0.620	6.20
10	10	500	78	1	10.039	2.61E+00	0.039	0.39
10	10	500	78	2	9.458	1.80E+00	0.542	5.42
10	10	500	78	3	9.749	3.77E+00	0.251	2.51
5	20	500	79	1	18.017	1.02E+01	1.983	9.92
5	20	500	79	2	16.121	8.35E+00	3.879	19.39
5	20	500	79	3	15.400	7.74E+00	4.600	23.00
10	20	500	79	1	ND	ND	ND	ND
10	20	500	79	2	ND	ND	ND	ND
10	20	500	79	3	ND	ND	ND	ND
5	30	500	80	1	11.549	2.26E+01	18.451	61.50
5	30	500	80	2	9.409	9.10E+00	20.591	68.64
5	30	500	80	3	7.355	6.26E+00	22.645	75.48
10	30	500	80	1	ND	ND	ND	ND
10	30	500	80	2	ND	ND	ND	ND
10	30	500	80	3	ND	ND	ND	ND
5	0	1000	81	1	0.036	3.73E-06	0.036	3.59
5	0	1000	81	2	0.034	6.86E-06	0.034	3.40
5	0	1000	81	3	0.038	5.88E-07	0.038	3.78
10	0	1000	81	1	ND	ND	ND	ND
10	0	1000	81	2	ND	ND	ND	ND
10	0	1000	81	3	ND	ND	ND	ND
5	0.1	1000	82	1	0.036	3.73E-06	0.064	6.41
5	0.1	1000	82	2	0.129	7.72E-06	0.029	29.27
5	0.1	1000	82	3	0.128	3.52E-06	0.028	28.10
10	0.1	1000	82	1	ND	ND	ND	ND
10	0.1	1000	82	2	ND	ND	ND	ND

10	0.1	1000	82	3	ND	ND	ND	ND
5	0.25	1000	83	1	0.259	3.13E-06	0.009	3.57
5	0.25	1000	83	2	0.259	4.13E-06	0.009	3.75
5	0.25	1000	83	3	0.257	6.32E-06	0.007	2.69
10	0.25	1000	83	1	ND	ND	ND	ND
10	0.25	1000	83	2	ND	ND	ND	ND
10	0.25	1000	83	3	ND	ND	ND	ND
5	0.5	1000	84	1	0.525	4.86E-04	0.025	5.08
5	0.5	1000	84	2	0.530	4.13E-04	0.030	5.93
5	0.5	1000	84	3	0.507	4.63E-04	0.007	1.38
10	0.5	1000	84	1	ND	ND	ND	ND
10	0.5	1000	84	2	ND	ND	ND	ND
10	0.5	1000	84	3	ND	ND	ND	ND
5	1	1000	85	1	1.030	5.36E-06	0.030	3.03
5	1	1000	85	2	1.037	7.20E-06	0.037	3.66
5	1	1000	85	3	1.024	3.52E-06	0.024	2.41
10	1	1000	85	1	ND	ND	ND	ND
10	1	1000	85	2	ND	ND	ND	ND
10	1	1000	85	3	ND	ND	ND	ND
5	2	1000	86	1	ND	ND	ND	ND
5	2	1000	86	2	ND	ND	ND	ND
5	2	1000	86	3	ND	ND	ND	ND
10	2	1000	86	1	ND	ND	ND	ND
10	2	1000	86	2	ND	ND	ND	ND
10	2	1000	86	3	ND	ND	ND	ND
5	5	1000	87	1	4.894	1.10E-05	0.106	2.12
5	5	1000	87	2	4.875	6.00E-06	0.125	2.50
5	5	1000	87	3	4.922	3.41E-05	0.078	1.55
10	5	1000	87	1	ND	ND	ND	ND
10	5	1000	87	2	ND	ND	ND	ND
10	5	1000	87	3	ND	ND	ND	ND
5	10	1000	88	1	9.274	2.69E-03	0.726	7.26
5	10	1000	88	2	9.157	4.75E-03	0.843	8.43
5	10	1000	88	3	9.392	6.28E-04	0.608	6.08
10	10	1000	88	1	ND	ND	ND	ND
10	10	1000	88	2	ND	ND	ND	ND
10	10	1000	88	3	ND	ND	ND	ND
5	20	1000	89	1	8.944	4.02E-02	11.056	55.28
5	20	1000	89	2	9.694	6.74E-02	10.306	51.53
5	20	1000	89	3	8.193	1.29E-02	11.807	59.03
10	20	1000	89	1	ND	ND	ND	ND
10	20	1000	89	2	ND	ND	ND	ND
10	20	1000	89	3	ND	ND	ND	ND
5	30	1000	90	1	11.478	3.01E-01	18.522	61.74
5	30	1000	90	2	11.362	1.42E-01	18.638	62.13
5	30	1000	90	3	10.966	5.03E-01	19.034	63.45

10	30	1000	90	1	ND	ND	ND	ND
10	30	1000	90	2	ND	ND	ND	ND
10	30	1000	90	3	ND	ND	ND	ND

Table A-2.

SUNA Path length (mm)	**NO_3-N** (mg L^{-1})	**SR NOM** (mg L^{-1})	**Matrix Cell**	**Replicate**	**NO_3-N Measurement** (mg L^{-1})	**Measurement Variance**	**Measurement Difference** (mg L^{-1})	**Measurement Error** (%)
5	0	0	1	1	0.0364	7.34E-06	0.036	3.639
5	0	0	1	2	0.0260	2.59E-06	0.026	2.604
5	0	0	1	3	0.0249	5.48E-06	0.025	2.491
10	0	0	1	1	-0.0176	2.31E-06	0.018	1.760
10	0	0	1	2	-0.0199	2.69E-06	0.020	1.990
10	0	0	1	3	-0.0199	3.48E-06	0.020	1.987
5	0.1	0	2	1	0.1182	5.29E-06	0.018	18.222
5	0.1	0	2	2	0.1132	3.15E-06	0.013	13.243
5	0.1	0	2	3	0.1112	2.57E-06	0.011	11.189
10	0.1	0	2	1	0.0838	2.56E-06	0.016	16.231
10	0.1	0	2	2	0.0838	2.00E-06	0.016	16.170
10	0.1	0	2	3	0.0826	2.30E-06	0.017	17.393
5	0.25	0	3	1	0.2832	1.50E-05	0.033	13.275
5	0.25	0	3	2	0.2691	3.13E-06	0.019	7.646
5	0.25	0	3	3	0.2673	2.56E-06	0.017	6.919
10	0.25	0	3	1	0.2467	1.18E-05	0.003	1.307
10	0.25	0	3	2	0.2426	9.45E-06	0.007	2.957
10	0.25	0	3	3	0.2401	4.09E-06	0.010	3.968
5	0.5	0	4	1	0.5464	1.02E-05	0.046	9.289
5	0.5	0	4	2	0.5287	4.93E-06	0.029	5.745
5	0.5	0	4	3	0.5310	4.47E-06	0.031	6.199
10	0.5	0	4	1	0.5054	4.85E-06	0.005	1.079
10	0.5	0	4	2	0.4963	3.13E-06	0.004	0.745
10	0.5	0	4	3	0.4904	5.29E-06	0.010	1.926
5	1	0	5	1	1.0254	4.93E-06	0.025	2.539
5	1	0	5	2	1.0173	3.14E-06	0.017	1.731
5	1	0	5	3	1.0017	4.28E-06	0.002	0.168
10	1	0	5	1	1.0030	6.60E-06	0.003	0.301
10	1	0	5	2	0.9936	6.16E-06	0.006	0.643
10	1	0	5	3	0.9805	8.23E-06	0.020	1.954
5	2	0	6	1	1.9926	8.26E-06	0.007	0.370
5	2	0	6	2	2.0024	4.99E-06	0.002	0.119
5	2	0	6	3	1.9884	5.55E-06	0.012	0.582
10	2	0	6	1	1.9973	4.54E-05	0.003	0.137

10	2	0	6	2	1.9790	2.06E-05	0.021	1.048
10	2	0	6	3	1.9852	2.35E-05	0.015	0.739
5	5	0	7	1	4.9378	4.63E-05	0.062	1.244
5	5	0	7	2	4.9437	3.91E-05	0.056	1.127
5	5	0	7	3	5.0219	2.64E-05	0.022	0.438
10	5	0	7	1	4.7955	1.45E-03	0.205	4.091
10	5	0	7	2	4.8007	1.39E-03	0.199	3.985
10	5	0	7	3	4.4126	5.59E-04	0.587	11.747
5	10	0	8	1	9.5132	8.33E-04	0.487	4.868
5	10	0	8	2	9.5303	1.22E-03	0.470	4.697
5	10	0	8	3	9.4648	1.54E-03	0.535	5.352
10	10	0	8	1	8.9667	7.98E-03	1.033	10.333
10	10	0	8	2	8.9450	8.34E-03	1.055	10.550
10	10	0	8	3	8.8865	7.74E-03	1.114	11.135
5	20	0	9	1	16.5847	5.66E-01	3.415	17.076
5	20	0	9	2	16.1285	5.60E-01	3.871	19.357
5	20	0	9	3	16.1507	3.46E-01	3.849	19.246
10	20	0	9	1	16.4793	4.26E-02	3.521	17.603
10	20	0	9	2	16.6305	5.51E-02	3.369	16.847
10	20	0	9	3	16.3801	2.08E-02	3.620	18.099
5	30	0	10	1	13.2296	2.39E+00	16.770	55.901
5	30	0	10	2	12.0325	1.47E+00	17.968	59.892
5	30	0	10	3	12.4144	1.57E+00	17.586	58.619
10	30	0	10	1	24.2926	5.80E-02	5.707	19.025
10	30	0	10	2	23.9846	3.87E-01	6.015	20.051
10	30	0	10	3	24.3728	1.17E-01	5.627	18.757
5	0	0.5	11	1	0.0238	3.44E-06	0.024	2.377
5	0	0.5	11	2	0.0202	1.80E-06	0.020	2.017
5	0	0.5	11	3	0.0165	3.05E-06	0.016	1.650
10	0	0.5	11	1	-0.0121	3.14E-06	0.012	1.214
10	0	0.5	11	2	-0.0119	5.36E-06	0.012	1.193
10	0	0.5	11	3	-0.0125	3.20E-06	0.013	1.253
5	0.1	0.5	12	1	0.1489	4.39E-06	0.049	48.935
5	0.1	0.5	12	2	0.1323	3.70E-06	0.032	32.255
5	0.1	0.5	12	3	0.1185	4.31E-06	0.018	18.487
10	0.1	0.5	12	1	0.0944	3.06E-06	0.006	5.614
10	0.1	0.5	12	2	0.0887	2.37E-06	0.011	11.303
10	0.1	0.5	12	3	0.0761	2.49E-06	0.024	23.859
5	0.25	0.5	13	1	0.2963	5.31E-05	0.046	18.531
5	0.25	0.5	13	2	0.2773	3.58E-06	0.027	10.939
5	0.25	0.5	13	3	0.2730	3.71E-06	0.023	9.202
10	0.25	0.5	13	1	0.2462	4.86E-06	0.004	1.515
10	0.25	0.5	13	2	0.2387	2.36E-06	0.011	4.538
10	0.25	0.5	13	3	0.2386	3.85E-06	0.011	4.573
5	0.5	0.5	14	1	0.5277	3.52E-06	0.028	5.531
5	0.5	0.5	14	2	0.5208	4.31E-06	0.021	4.166

5	0.5	0.5	14	3	0.5191	5.65E-06	0.019	3.824
10	0.5	0.5	14	1	0.5065	6.98E-06	0.007	1.308
10	0.5	0.5	14	2	0.5113	5.02E-06	0.011	2.259
10	0.5	0.5	14	3	0.4985	3.37E-06	0.002	0.307
5	1	0.5	15	1	1.0242	4.70E-06	0.024	2.421
5	1	0.5	15	2	1.0150	4.34E-06	0.015	1.501
5	1	0.5	15	3	1.0136	3.96E-06	0.014	1.360
10	1	0.5	15	1	0.9968	7.95E-06	0.003	0.323
10	1	0.5	15	2	0.9930	7.56E-06	0.007	0.705
10	1	0.5	15	3	0.9912	1.05E-05	0.009	0.876
5	2	0.5	16	1	1.9867	5.60E-06	0.013	0.665
5	2	0.5	16	2	1.9954	7.28E-06	0.005	0.231
5	2	0.5	16	3	1.9868	7.99E-06	0.013	0.662
10	2	0.5	16	1	1.9565	2.81E-05	0.043	2.174
10	2	0.5	16	2	1.9432	2.94E-05	0.057	2.841
10	2	0.5	16	3	1.9383	1.84E-05	0.062	3.087
5	5	0.5	17	1	4.9441	4.45E-05	0.056	1.118
5	5	0.5	17	2	4.9237	4.27E-05	0.076	1.527
5	5	0.5	17	3	4.8724	2.77E-05	0.128	2.553
10	5	0.5	17	1	4.7533	6.34E-04	0.247	4.935
10	5	0.5	17	2	4.7176	1.06E-03	0.282	5.649
10	5	0.5	17	3	4.6902	1.40E-03	0.310	6.197
5	10	0.5	18	1	9.4826	1.32E-03	0.517	5.174
5	10	0.5	18	2	9.5055	1.50E-03	0.495	4.945
5	10	0.5	18	3	9.4818	1.67E-03	0.518	5.182
10	10	0.5	18	1	9.4138	3.67E-02	0.586	5.862
10	10	0.5	18	2	9.1014	7.33E-03	0.899	8.986
10	10	0.5	18	3	9.3255	3.16E-02	0.674	6.745
5	20	0.5	19	1	16.3638	4.41E-01	3.636	18.181
5	20	0.5	19	2	15.8442	4.03E-01	4.156	20.779
5	20	0.5	19	3	15.6716	2.88E-01	4.328	21.642
10	20	0.5	19	1	16.1032	2.12E-01	3.897	19.484
10	20	0.5	19	2	15.6035	3.31E-02	4.397	21.983
10	20	0.5	19	3	16.6655	2.84E-02	3.335	16.673
5	30	0.5	20	1	14.1196	3.63E+00	15.880	52.935
5	30	0.5	20	2	12.9432	1.88E+00	17.057	56.856
5	30	0.5	20	3	11.9572	2.33E+00	18.043	60.143
10	30	0.5	20	1	24.5333	1.31E-01	5.467	18.222
10	30	0.5	20	2	24.3657	2.83E-01	5.634	18.781
10	30	0.5	20	3	23.6449	7.05E-02	6.355	21.184
5	0	1	21	1	0.0344	4.52E-06	0.034	3.437
5	0	1	21	2	0.0239	4.80E-06	0.024	2.394
5	0	1	21	3	0.0203	3.33E-06	0.020	2.028
10	0	1	21	1	-0.0168	2.86E-06	0.017	1.682
10	0	1	21	2	-0.0209	4.17E-06	0.021	2.092
10	0	1	21	3	-0.0210	5.41E-06	0.021	2.102

5	0.1	1	22	1	0.1275	2.43E-06	0.027	27.478
5	0.1	1	22	2	0.1195	3.55E-06	0.020	19.544
5	0.1	1	22	3	0.1210	3.73E-06	0.021	20.961
10	0.1	1	22	1	0.0957	2.75E-06	0.004	4.305
10	0.1	1	22	2	0.0832	3.38E-06	0.017	16.845
10	0.1	1	22	3	0.0838	3.54E-06	0.016	16.222
5	0.25	1	23	1	0.2649	3.36E-06	0.015	5.973
5	0.25	1	23	2	0.2617	5.04E-06	0.012	4.667
5	0.25	1	23	3	0.2592	3.40E-06	0.009	3.666
10	0.25	1	23	1	0.2380	4.69E-06	0.012	4.802
10	0.25	1	23	2	0.2367	3.86E-06	0.013	5.314
10	0.25	1	23	3	0.2355	3.54E-06	0.014	5.788
5	0.5	1	24	1	0.5306	3.22E-06	0.031	6.117
5	0.5	1	24	2	0.5233	4.52E-06	0.023	4.667
5	0.5	1	24	3	0.5310	6.37E-06	0.031	6.205
10	0.5	1	24	1	0.5039	6.69E-06	0.004	0.770
10	0.5	1	24	2	0.5053	4.34E-06	0.005	1.053
10	0.5	1	24	3	0.5054	2.89E-05	0.005	1.088
5	1	1	25	1	1.0228	5.14E-06	0.023	2.276
5	1	1	25	2	1.0570	5.87E-06	0.057	5.702
5	1	1	25	3	1.0388	5.21E-06	0.039	3.882
10	1	1	25	1	1.0124	1.08E-05	0.012	1.242
10	1	1	25	2	0.9775	1.33E-05	0.022	2.247
10	1	1	25	3	0.9891	9.45E-06	0.011	1.093
5	2	1	26	1	2.0265	6.00E-06	0.027	1.327
5	2	1	26	2	2.0060	5.70E-06	0.006	0.301
5	2	1	26	3	2.0027	7.57E-06	0.003	0.136
10	2	1	26	1	1.9604	6.52E-02	0.040	1.980
10	2	1	26	2	1.9629	5.36E-05	0.037	1.855
10	2	1	26	3	1.9447	3.31E-05	0.055	2.767
5	5	1	27	1	4.9225	4.46E-05	0.077	1.550
5	5	1	27	2	4.9297	4.00E-05	0.070	1.406
5	5	1	27	3	4.8978	5.13E-05	0.102	2.044
10	5	1	27	1	4.6935	4.98E-03	0.307	6.130
10	5	1	27	2	4.5846	2.87E-03	0.415	8.308
10	5	1	27	3	4.5229	4.37E-03	0.477	9.543
5	10	1	28	1	9.5267	1.95E-03	0.473	4.733
5	10	1	28	2	9.5117	8.53E-04	0.488	4.883
5	10	1	28	3	9.5968	1.94E-03	0.403	4.032
10	10	1	28	1	8.9921	9.77E-03	1.008	10.079
10	10	1	28	2	8.7863	8.96E-03	1.214	12.137
10	10	1	28	3	8.9109	5.77E-03	1.089	10.891
5	20	1	29	1	16.5185	5.07E-01	3.481	17.407
5	20	1	29	2	16.0786	4.29E-01	3.921	19.607
5	20	1	29	3	15.9785	5.21E-01	4.022	20.108
10	20	1	29	1	16.3743	9.19E-02	3.626	18.128

10	20	1	29	2	16.4466	6.45E-02	3.553	17.767
10	20	1	29	3	16.2828	3.40E-02	3.717	18.586
5	30	1	30	1	14.1518	3.36E+00	15.848	52.827
5	30	1	30	2	13.4287	3.00E+00	16.571	55.238
5	30	1	30	3	13.0350	3.49E+00	16.965	56.550
10	30	1	30	1	24.4782	7.48E-02	5.522	18.406
10	30	1	30	2	24.4851	8.37E-02	5.515	18.383
10	30	1	30	3	24.4656	1.68E-01	5.534	18.448
5	0	2	31	1	0.0211	5.10E-06	0.021	2.106
5	0	2	31	2	0.0173	3.30E-06	0.017	1.728
5	0	2	31	3	0.0157	4.39E-06	0.016	1.567
10	0	2	31	1	-0.0138	4.75E-06	0.014	1.376
10	0	2	31	2	-0.0159	2.70E-06	0.016	1.589
10	0	2	31	3	-0.0171	2.88E-06	0.017	1.707
5	0.1	2	32	1	0.1236	5.08E-06	0.024	23.606
5	0.1	2	32	2	0.1194	3.95E-06	0.019	19.359
5	0.1	2	32	3	0.1181	2.02E-06	0.018	18.076
10	0.1	2	32	1	0.0863	4.10E-06	0.014	13.744
10	0.1	2	32	2	0.0837	3.33E-06	0.016	16.330
10	0.1	2	32	3	0.0804	3.81E-06	0.020	19.592
5	0.25	2	33	1	0.2758	3.76E-06	0.026	10.324
5	0.25	2	33	2	0.2736	3.57E-06	0.024	9.429
5	0.25	2	33	3	0.2701	3.99E-06	0.020	8.025
10	0.25	2	33	1	0.2423	4.79E-06	0.008	3.095
10	0.25	2	33	2	0.2400	4.01E-06	0.010	4.019
10	0.25	2	33	3	0.2384	4.89E-06	0.012	4.648
5	0.5	2	34	1	0.5487	5.42E-06	0.049	9.748
5	0.5	2	34	2	0.5313	5.38E-06	0.031	6.255
5	0.5	2	34	3	0.5264	3.64E-06	0.026	5.285
10	0.5	2	34	1	0.5045	6.26E-06	0.004	0.894
10	0.5	2	34	2	0.4964	5.52E-06	0.004	0.716
10	0.5	2	34	3	0.4966	4.22E-06	0.003	0.684
5	1	2	35	1	1.0499	5.72E-06	0.050	4.992
5	1	2	35	2	1.0323	5.38E-06	0.032	3.234
5	1	2	35	3	1.0306	3.47E-06	0.031	3.058
10	1	2	35	1	1.0258	9.08E-06	0.026	2.579
10	1	2	35	2	1.0116	1.06E-05	0.012	1.161
10	1	2	35	3	1.0050	1.03E-05	0.005	0.499
5	2	2	36	1	1.9991	8.27E-06	0.001	0.044
5	2	2	36	2	1.9890	4.37E-06	0.011	0.549
5	2	2	36	3	1.9883	7.13E-06	0.012	0.587
10	2	2	36	1	1.9794	5.24E-05	0.021	1.030
10	2	2	36	2	1.9574	3.27E-05	0.043	2.131
10	2	2	36	3	1.9816	3.16E-05	0.018	0.918
5	5	2	37	1	4.9325	4.91E-05	0.068	1.351
5	5	2	37	2	5.0354	5.13E-05	0.035	0.708

5	5	2	37	3	5.0610	5.66E-05	0.061	1.220
10	5	2	37	1	4.7645	2.39E-03	0.236	4.710
10	5	2	37	2	4.6864	2.45E-03	0.314	6.271
10	5	2	37	3	4.6697	2.77E-03	0.330	6.606
5	10	2	38	1	9.5491	1.52E-03	0.451	4.509
5	10	2	38	2	9.5179	1.50E-03	0.482	4.821
5	10	2	38	3	9.5839	1.38E-03	0.416	4.161
10	10	2	38	1	8.9933	5.19E-03	1.007	10.067
10	10	2	38	2	9.0179	4.32E-03	0.982	9.821
10	10	2	38	3	8.9890	8.69E-03	1.011	10.110
5	20	2	39	1	16.2824	4.28E-01	3.718	18.588
5	20	2	39	2	16.2402	7.08E-01	3.760	18.799
5	20	2	39	3	15.9377	4.29E-01	4.062	20.311
10	20	2	39	1	16.8088	1.01E-01	3.191	15.956
10	20	2	39	2	16.2716	3.87E-02	3.728	18.642
10	20	2	39	3	16.5804	4.16E-02	3.420	17.098
5	30	2	40	1	14.7323	5.33E+00	15.268	50.892
5	30	2	40	2	13.1033	3.78E+00	16.897	56.322
5	30	2	40	3	12.6164	3.40E+00	17.384	57.945
10	30	2	40	1	24.4483	9.94E-02	5.552	18.506
10	30	2	40	2	24.1907	2.39E-01	5.809	19.364
10	30	2	40	3	23.6806	8.01E-02	6.319	21.065
5	0	5	41	1	0.0286	3.57E-06	0.029	2.859
5	0	5	41	2	0.0229	3.26E-06	0.023	2.288
5	0	5	41	3	0.0189	4.53E-06	0.019	1.887
10	0	5	41	1	-0.0110	4.82E-06	0.011	1.101
10	0	5	41	2	-0.0150	5.38E-06	0.015	1.499
10	0	5	41	3	-0.0165	3.84E-06	0.017	1.653
5	0.1	5	42	1	0.1141	4.62E-06	0.014	14.132
5	0.1	5	42	2	0.1227	5.50E-06	0.023	22.709
5	0.1	5	42	3	0.1238	5.46E-06	0.024	23.802
10	0.1	5	42	1	0.0930	1.53E-04	0.007	7.033
10	0.1	5	42	2	0.0907	4.81E-06	0.009	9.276
10	0.1	5	42	3	0.0949	3.61E-06	0.005	5.071
5	0.25	5	43	1	0.2747	4.80E-06	0.025	9.889
5	0.25	5	43	2	0.2720	3.71E-06	0.022	8.785
5	0.25	5	43	3	0.2630	5.35E-06	0.013	5.213
10	0.25	5	43	1	0.2427	6.97E-06	0.007	2.904
10	0.25	5	43	2	0.2379	9.12E-06	0.012	4.844
10	0.25	5	43	3	0.2461	8.02E-06	0.004	1.569
5	0.5	5	44	1	0.5482	9.47E-06	0.048	9.649
5	0.5	5	44	2	0.5335	6.81E-06	0.033	6.695
5	0.5	5	44	3	0.5303	4.70E-06	0.030	6.066
10	0.5	5	44	1	0.5097	6.07E-06	0.010	1.938
10	0.5	5	44	2	0.4957	5.93E-06	0.004	0.863
10	0.5	5	44	3	0.4988	8.04E-06	0.001	0.246

5	1	5	45	1	1.0294	1.43E-05	0.029	2.941
5	1	5	45	2	1.0186	6.97E-06	0.019	1.858
5	1	5	45	3	1.0174	7.74E-06	0.017	1.736
10	1	5	45	1	1.0082	1.64E-05	0.008	0.816
10	1	5	45	2	1.0121	1.13E-05	0.012	1.209
10	1	5	45	3	1.0061	1.19E-05	0.006	0.613
5	2	5	46	1	1.9901	1.35E-05	0.010	0.493
5	2	5	46	2	1.9853	8.01E-06	0.015	0.734
5	2	5	46	3	1.9756	1.10E-05	0.024	1.221
10	2	5	46	1	1.9803	5.86E-05	0.020	0.986
10	2	5	46	2	1.9726	5.16E-05	0.027	1.368
10	2	5	46	3	1.9616	4.41E-05	0.038	1.919
5	5	5	47	1	4.9356	7.64E-05	0.064	1.289
5	5	5	47	2	4.9586	5.67E-05	0.041	0.828
5	5	5	47	3	4.9238	4.48E-05	0.076	1.523
10	5	5	47	1	4.7541	1.54E-03	0.246	4.917
10	5	5	47	2	4.7322	1.95E-03	0.268	5.356
10	5	5	47	3	4.7306	2.61E-03	0.269	5.387
5	10	5	48	1	9.5772	2.18E-03	0.423	4.228
5	10	5	48	2	9.5136	1.68E-03	0.486	4.864
5	10	5	48	3	9.4969	1.84E-03	0.503	5.031
10	10	5	48	1	8.9931	9.97E-03	1.007	10.069
10	10	5	48	2	9.0555	8.58E-03	0.945	9.445
10	10	5	48	3	9.0632	7.48E-03	0.937	9.368
5	20	5	49	1	15.8953	3.42E-01	4.105	20.523
5	20	5	49	2	16.6783	8.45E-01	3.322	16.608
5	20	5	49	3	15.9496	3.89E-01	4.050	20.252
10	20	5	49	1	15.6419	6.32E-01	4.358	21.790
10	20	5	49	2	17.1148	3.73E-02	2.885	14.426
10	20	5	49	3	15.2647	1.98E-01	4.735	23.676
5	30	5	50	1	15.0265	9.69E+00	14.974	49.912
5	30	5	50	2	12.7795	3.29E+00	17.221	57.402
5	30	5	50	3	13.5384	4.66E+00	16.462	54.872
10	30	5	50	1	24.2228	1.04E-01	5.777	19.257
10	30	5	50	2	25.3772	2.22E-01	4.623	15.409
10	30	5	50	3	24.9166	3.95E-01	5.083	16.945
5	0	10	51	1	0.0208	5.70E-06	0.021	2.084
5	0	10	51	2	0.0170	4.67E-06	0.017	1.704
5	0	10	51	3	0.0165	7.18E-06	0.016	1.646
10	0	10	51	1	-0.0105	6.11E-06	0.010	1.047
10	0	10	51	2	-0.0124	7.67E-06	0.012	1.239
10	0	10	51	3	-0.0113	7.64E-06	0.011	1.132
5	0.1	10	52	1	0.1701	7.80E-06	0.070	70.148
5	0.1	10	52	2	0.1325	5.18E-06	0.032	32.462
5	0.1	10	52	3	0.1221	5.71E-06	0.022	22.056
10	0.1	10	52	1	0.1439	6.53E-06	0.044	43.932

10	0.1	10	52	2	0.0922	9.91E-06	0.008	7.815
10	0.1	10	52	3	0.0891	1.05E-05	0.011	10.942
5	0.25	10	53	1	0.2780	4.68E-06	0.028	11.182
5	0.25	10	53	2	0.2736	4.29E-06	0.024	9.430
5	0.25	10	53	3	0.2707	6.36E-06	0.021	8.297
10	0.25	10	53	1	0.2501	1.56E-05	0.000	0.043
10	0.25	10	53	2	0.2467	8.59E-06	0.003	1.319
10	0.25	10	53	3	0.2427	1.11E-05	0.007	2.925
5	0.5	10	54	1	0.5319	1.05E-05	0.032	6.386
5	0.5	10	54	2	0.5274	7.56E-06	0.027	5.477
5	0.5	10	54	3	0.5208	5.18E-06	0.021	4.150
10	0.5	10	54	1	0.5037	1.24E-05	0.004	0.742
10	0.5	10	54	2	0.5008	1.16E-05	0.001	0.161
10	0.5	10	54	3	0.4959	2.50E-05	0.004	0.811
5	1	10	55	1	1.0237	8.52E-06	0.024	2.368
5	1	10	55	2	1.0416	7.13E-06	0.042	4.159
5	1	10	55	3	1.0296	9.00E-06	0.030	2.959
10	1	10	55	1	1.0015	2.05E-05	0.001	0.147
10	1	10	55	2	1.0182	1.83E-05	0.018	1.822
10	1	10	55	3	0.9902	1.93E-05	0.010	0.984
5	2	10	56	1	1.9601	1.36E-05	0.040	1.994
5	2	10	56	2	1.9565	1.22E-05	0.044	2.177
5	2	10	56	3	1.9697	1.31E-05	0.030	1.515
10	2	10	56	1	1.9485	7.55E-05	0.051	2.574
10	2	10	56	2	1.9450	8.36E-05	0.055	2.752
10	2	10	56	3	1.9617	7.84E-05	0.038	1.914
5	5	10	57	1	4.9707	7.77E-05	0.029	0.587
5	5	10	57	2	4.9509	6.37E-05	0.049	0.983
5	5	10	57	3	4.9308	1.01E-04	0.069	1.384
10	5	10	57	1	4.7735	1.19E-03	0.227	4.530
10	5	10	57	2	4.6651	1.17E-03	0.335	6.699
10	5	10	57	3	4.6430	2.81E-03	0.357	7.140
5	10	10	58	1	9.5387	2.74E-03	0.461	4.613
5	10	10	58	2	9.5354	2.76E-03	0.465	4.646
5	10	10	58	3	9.4805	2.10E-03	0.520	5.195
10	10	10	58	1	9.0905	1.25E-02	0.910	9.095
10	10	10	58	2	9.8240	1.55E-02	0.176	1.760
10	10	10	58	3	9.4112	1.39E-02	0.589	5.888
5	20	10	59	1	16.3935	7.40E-01	3.606	18.032
5	20	10	59	2	15.4557	5.84E-01	4.544	22.722
5	20	10	59	3	15.6990	8.52E-01	4.301	21.505
10	20	10	59	1	17.3576	8.81E-02	2.642	13.212
10	20	10	59	2	18.8842	3.30E-02	1.116	5.579
10	20	10	59	3	18.9572	9.77E-02	1.043	5.214
5	30	10	60	1	15.1649	1.24E+01	14.835	49.450
5	30	10	60	2	13.8816	7.68E+00	16.118	53.728

5	30	10	60	3	12.3977	1.74E+00	17.602	58.674
10	30	10	60	1	24.3977	3.55E-01	5.602	18.674
10	30	10	60	2	24.8732	1.66E-01	5.127	17.089
10	30	10	60	3	24.9769	1.55E-01	5.023	16.744
5	0	20	61	1	0.0134	1.09E-05	0.013	1.342
5	0	20	61	2	0.0113	9.80E-06	0.011	1.125
5	0	20	61	3	0.0107	1.15E-05	0.011	1.074
10	0	20	61	1	-0.0109	2.01E-05	0.011	1.086
10	0	20	61	2	-0.0159	2.42E-05	0.016	1.586
10	0	20	61	3	-0.0162	2.48E-05	0.016	1.624
5	0.1	20	62	1	0.1511	9.05E-06	0.051	51.076
5	0.1	20	62	2	0.1296	1.45E-05	0.030	29.609
5	0.1	20	62	3	0.1222	8.88E-06	0.022	22.196
10	0.1	20	62	1	0.1062	1.95E-05	0.006	6.186
10	0.1	20	62	2	0.1055	2.65E-05	0.006	5.536
10	0.1	20	62	3	0.0924	3.27E-05	0.008	7.639
5	0.25	20	63	1	0.2698	9.81E-06	0.020	7.933
5	0.25	20	63	2	0.2635	7.74E-06	0.014	5.407
5	0.25	20	63	3	0.2656	1.26E-05	0.016	6.242
10	0.25	20	63	1	0.2449	3.86E-05	0.005	2.022
10	0.25	20	63	2	0.2603	4.58E-05	0.010	4.111
10	0.25	20	63	3	0.2480	1.07E-04	0.002	0.807
5	0.5	20	64	1	0.5183	7.67E-06	0.018	3.664
5	0.5	20	64	2	0.5163	1.25E-05	0.016	3.260
5	0.5	20	64	3	0.5140	9.63E-06	0.014	2.803
10	0.5	20	64	1	0.5045	5.75E-05	0.005	0.905
10	0.5	20	64	2	0.4961	9.71E-05	0.004	0.790
10	0.5	20	64	3	0.4924	4.54E-05	0.008	1.530
5	1	20	65	1	1.0056	9.62E-06	0.006	0.563
5	1	20	65	2	1.0142	6.07E-06	0.014	1.424
5	1	20	65	3	1.0241	1.00E-05	0.024	2.407
10	1	20	65	1	0.9904	2.06E-05	0.010	0.965
10	1	20	65	2	0.9980	2.51E-05	0.002	0.197
10	1	20	65	3	1.0133	3.18E-05	0.013	1.334
5	2	20	66	1	1.9622	1.74E-05	0.038	1.890
5	2	20	66	2	1.9778	1.58E-05	0.022	1.111
5	2	20	66	3	1.9725	1.94E-05	0.027	1.373
10	2	20	66	1	1.9278	6.98E-04	0.072	3.612
10	2	20	66	2	1.9554	2.47E-04	0.045	2.230
10	2	20	66	3	1.9477	4.04E-04	0.052	2.613
5	5	20	67	1	4.9144	1.49E-04	0.086	1.712
5	5	20	67	2	4.9412	1.35E-04	0.059	1.175
5	5	20	67	3	4.9107	1.79E-04	0.089	1.786
10	5	20	67	1	4.6848	2.81E-03	0.315	6.305
10	5	20	67	2	4.6473	2.59E-03	0.353	7.054
10	5	20	67	3	4.6980	8.55E-03	0.302	6.041

5	10	20	68	1	9.4849	4.62E-03	0.515	5.151
5	10	20	68	2	9.5495	4.11E-03	0.450	4.505
5	10	20	68	3	9.3695	3.00E-03	0.631	6.305
10	10	20	68	1	9.4604	4.46E-02	0.540	5.396
10	10	20	68	2	8.7353	2.16E-02	1.265	12.647
10	10	20	68	3	8.7855	1.23E-02	1.215	12.145
5	20	20	69	1	15.7076	9.69E-01	4.292	21.462
5	20	20	69	2	15.4278	9.66E-01	4.572	22.861
5	20	20	69	3	15.1279	9.61E-01	4.872	24.361
10	20	20	69	1	17.2342	1.17E-01	2.766	13.829
10	20	20	69	2	17.1986	1.15E-01	2.801	14.007
10	20	20	69	3	17.1897	7.47E-02	2.810	14.052
5	30	20	70	1	11.8819	4.12E+00	18.118	60.394
5	30	20	70	2	10.1885	3.07E+00	19.812	66.038
5	30	20	70	3	10.5840	2.64E+00	19.416	64.720
10	30	20	70	1	24.2782	5.13E-01	5.722	19.073
10	30	20	70	2	24.0139	7.33E-01	5.986	19.954
10	30	20	70	3	24.4447	5.77E-01	5.555	18.518
5	0	40	71	1	0.0294	4.84E-05	0.029	2.943
5	0	40	71	2	0.0146	2.92E-05	0.015	1.461
5	0	40	71	3	0.0113	3.49E-05	0.011	1.126
10	0	40	71	1	0.0040	1.55E-04	0.004	0.402
10	0	40	71	2	-0.0026	2.24E-04	0.003	0.260
10	0	40	71	3	0.0003	2.03E-04	0.000	0.028
5	0.1	40	72	1	0.1150	3.44E-05	0.015	14.991
5	0.1	40	72	2	0.1220	4.16E-05	0.022	21.967
5	0.1	40	72	3	0.1192	3.53E-05	0.019	19.229
10	0.1	40	72	1	0.0765	2.45E-04	0.023	23.495
10	0.1	40	72	2	0.0887	2.24E-04	0.011	11.313
10	0.1	40	72	3	0.0652	5.04E-04	0.035	34.785
5	0.25	40	73	1	0.2544	3.61E-05	0.004	1.754
5	0.25	40	73	2	0.2522	3.87E-05	0.002	0.887
5	0.25	40	73	3	0.2535	3.20E-05	0.003	1.397
10	0.25	40	73	1	0.2359	1.88E-04	0.014	5.635
10	0.25	40	73	2	0.2322	1.48E-04	0.018	7.113
10	0.25	40	73	3	0.2297	1.78E-04	0.020	8.116
5	0.5	40	74	1	0.5088	3.60E-05	0.009	1.767
5	0.5	40	74	2	0.5103	2.65E-05	0.010	2.059
5	0.5	40	74	3	0.5025	3.51E-05	0.002	0.497
10	0.5	40	74	1	0.4862	3.05E-04	0.014	2.755
10	0.5	40	74	2	0.5635	1.12E-03	0.064	12.709
10	0.5	40	74	3	0.4872	5.35E-04	0.013	2.562
5	1	40	75	1	1.0025	3.75E-05	0.002	0.249
5	1	40	75	2	1.0034	2.68E-05	0.003	0.341
5	1	40	75	3	1.0000	3.91E-05	0.000	0.001
10	1	40	75	1	0.9812	7.32E-04	0.019	1.880

10	1	40	75	2	0.8663	1.17E-03	0.134	13.374
10	1	40	75	3	0.9955	1.10E-03	0.004	0.450
5	2	40	76	1	2.0007	5.90E-05	0.001	0.033
5	2	40	76	2	1.9983	5.05E-05	0.002	0.087
5	2	40	76	3	1.9660	5.39E-05	0.034	1.700
10	2	40	76	1	1.9574	5.44E-03	0.043	2.131
10	2	40	76	2	1.9269	6.85E-03	0.073	3.654
10	2	40	76	3	1.9112	4.01E-03	0.089	4.441
5	5	40	77	1	4.9250	5.14E-04	0.075	1.500
5	5	40	77	2	5.0097	5.22E-04	0.010	0.194
5	5	40	77	3	4.9145	3.83E-04	0.086	1.711
10	5	40	77	1	4.7846	2.24E-02	0.215	4.308
10	5	40	77	2	4.5892	1.95E-02	0.411	8.215
10	5	40	77	3	4.4498	1.96E-02	0.550	11.005
5	10	40	78	1	9.4296	1.77E-02	0.570	5.704
5	10	40	78	2	9.4208	1.39E-02	0.579	5.792
5	10	40	78	3	9.4024	1.70E-02	0.598	5.976
10	10	40	78	1	8.7206	5.54E-02	1.279	12.794
10	10	40	78	2	8.9056	7.04E-02	1.094	10.944
10	10	40	78	3	8.9075	1.26E-01	1.093	10.925
5	20	40	79	1	14.4868	2.23E+00	5.513	27.566
5	20	40	79	2	16.8471	7.22E+00	3.153	15.764
5	20	40	79	3	15.0434	2.59E+00	4.957	24.783
10	20	40	79	1	16.9773	1.20E+00	3.023	15.113
10	20	40	79	2	16.9858	7.14E-01	3.014	15.071
10	20	40	79	3	16.9373	9.33E-01	3.063	15.313
5	30	40	80	1	10.1501	7.82E+00	19.850	66.166
5	30	40	80	2	8.4262	4.81E+00	21.574	71.913
5	30	40	80	3	11.0546	1.69E+01	18.945	63.151
10	30	40	80	1	24.9245	4.66E+00	5.075	16.918
10	30	40	80	2	25.9145	2.65E+00	4.086	13.618
10	30	40	80	3	24.8456	4.51E+00	5.154	17.181
5	0	80	81	1	-0.0143	2.01E-04	0.014	1.433
5	0	80	81	2	-0.0017	2.81E-04	0.002	0.172
5	0	80	81	3	0.0015	3.28E-04	0.002	0.152
10	0	80	81	1	ND	ND	ND	ND
10	0	80	81	2	ND	ND	ND	ND
10	0	80	81	3	ND	ND	ND	ND
5	0.1	80	82	1	0.1093	2.35E-04	0.009	9.306
5	0.1	80	82	2	0.1082	3.38E-04	0.008	8.167
5	0.1	80	82	3	0.1105	2.61E-04	0.011	10.500
10	0.1	80	82	1	ND	ND	ND	ND
10	0.1	80	82	2	ND	ND	ND	ND
10	0.1	80	82	3	ND	ND	ND	ND
5	0.25	80	83	1	0.2716	2.13E-04	0.022	8.656
5	0.25	80	83	2	0.2669	1.49E-04	0.017	6.758

5	0.25	80	83	3	0.2549	2.88E-04	0.005	1.942
10	0.25	80	83	1	ND	ND	ND	ND
10	0.25	80	83	2	ND	ND	ND	ND
10	0.25	80	83	3	ND	ND	ND	ND
5	0.5	80	84	1	0.5035	4.32E-04	0.003	0.693
5	0.5	80	84	2	0.4935	2.82E-04	0.007	1.306
5	0.5	80	84	3	0.4995	4.04E-04	0.000	0.092
10	0.5	80	84	1	ND	ND	ND	ND
10	0.5	80	84	2	ND	ND	ND	ND
10	0.5	80	84	3	ND	ND	ND	ND
5	1	80	85	1	1.0038	4.67E-04	0.004	0.380
5	1	80	85	2	0.9868	3.88E-04	0.013	1.319
5	1	80	85	3	0.9893	3.03E-04	0.011	1.068
10	1	80	85	1	ND	ND	ND	ND
10	1	80	85	2	ND	ND	ND	ND
10	1	80	85	3	ND	ND	ND	ND
5	2	80	86	1	2.0032	6.98E-04	0.003	0.159
5	2	80	86	2	1.9439	6.34E-04	0.056	2.807
5	2	80	86	3	1.9574	6.44E-04	0.043	2.132
10	2	80	86	1	ND	ND	ND	ND
10	2	80	86	2	ND	ND	ND	ND
10	2	80	86	3	ND	ND	ND	ND
5	5	80	87	1	4.9109	5.13E-03	0.089	1.783
5	5	80	87	2	4.9034	5.62E-03	0.097	1.933
5	5	80	87	3	4.8913	4.41E-03	0.109	2.175
10	5	80	87	1	ND	ND	ND	ND
10	5	80	87	2	ND	ND	ND	ND
10	5	80	87	3	ND	ND	ND	ND
5	10	80	88	1	9.5487	2.09E-01	0.451	4.513
5	10	80	88	2	9.2824	2.14E-01	0.718	7.176
5	10	80	88	3	9.1274	1.96E-01	0.873	8.726
10	10	80	88	1	ND	ND	ND	ND
10	10	80	88	2	ND	ND	ND	ND
10	10	80	88	3	ND	ND	ND	ND
5	20	80	89	1	12.2461	9.46E+00	7.754	38.769
5	20	80	89	2	13.0424	1.42E+01	6.958	34.788
5	20	80	89	3	13.0020	1.24E+01	6.998	34.990
10	20	80	89	1	ND	ND	ND	ND
10	20	80	89	2	ND	ND	ND	ND
10	20	80	89	3	ND	ND	ND	ND
5	30	80	90	1	8.7203	2.86E+01	21.280	70.932
5	30	80	90	2	7.8155	2.14E+01	22.184	73.948
5	30	80	90	3	6.4910	1.76E+01	23.509	78.363
10	30	80	90	1	ND	ND	ND	ND
10	30	80	90	2	ND	ND	ND	ND
10	30	80	90	3	ND	ND	ND	ND

5	0	100	91	1	0.1107	4.37E-03	0.111	11.068
5	0	100	91	2	0.1079	7.86E-03	0.108	10.794
5	0	100	91	3	0.1143	6.56E-03	0.114	11.426
10	0	100	91	1	ND	ND	ND	ND
10	0	100	91	2	ND	ND	ND	ND
10	0	100	91	3	ND	ND	ND	ND
5	0.1	100	92	1	0.1803	6.76E-03	0.080	80.346
5	0.1	100	92	2	0.2091	6.58E-03	0.109	109.140
5	0.1	100	92	3	0.1887	8.83E-03	0.089	88.720
10	0.1	100	92	1	ND	ND	ND	ND
10	0.1	100	92	2	ND	ND	ND	ND
10	0.1	100	92	3	ND	ND	ND	ND
5	0.25	100	93	1	0.3541	4.65E-03	0.104	41.636
5	0.25	100	93	2	0.3467	6.01E-03	0.097	38.692
5	0.25	100	93	3	0.3692	4.77E-03	0.119	47.666
10	0.25	100	93	1	ND	ND	ND	ND
10	0.25	100	93	2	ND	ND	ND	ND
10	0.25	100	93	3	ND	ND	ND	ND
5	0.5	100	94	1	0.6082	8.34E-03	0.108	21.647
5	0.5	100	94	2	0.5854	6.44E-03	0.085	17.087
5	0.5	100	94	3	0.6151	6.97E-03	0.115	23.021
10	0.5	100	94	1	ND	ND	ND	ND
10	0.5	100	94	2	ND	ND	ND	ND
10	0.5	100	94	3	ND	ND	ND	ND
5	1	100	95	1	1.0991	7.59E-03	0.099	9.914
5	1	100	95	2	1.1365	1.35E-02	0.136	13.645
5	1	100	95	3	1.1221	1.10E-02	0.122	12.212
10	1	100	95	1	ND	ND	ND	ND
10	1	100	95	2	ND	ND	ND	ND
10	1	100	95	3	ND	ND	ND	ND
5	2	100	96	1	2.0985	2.87E-02	0.099	4.926
5	2	100	96	2	2.0918	2.21E-02	0.092	4.590
5	2	100	96	3	2.0022	2.16E-02	0.002	0.112
10	2	100	96	1	ND	ND	ND	ND
10	2	100	96	2	ND	ND	ND	ND
10	2	100	96	3	ND	ND	ND	ND
5	5	100	97	1	4.8862	1.78E-01	0.114	2.276
5	5	100	97	2	4.5971	1.59E-01	0.403	8.058
5	5	100	97	3	4.5234	1.76E-01	0.477	9.532
10	5	100	97	1	ND	ND	ND	ND
10	5	100	97	2	ND	ND	ND	ND
10	5	100	97	3	ND	ND	ND	ND
5	10	100	98	1	7.7911	2.19E+00	2.209	22.089
5	10	100	98	2	6.8111	1.91E+00	3.189	31.889
5	10	100	98	3	6.4268	1.50E+00	3.573	35.732
10	10	100	98	1	ND	ND	ND	ND

10	10	100	98	2	ND	ND	ND	ND
10	10	100	98	3	ND	ND	ND	ND
5	20	100	99	1	7.0357	1.75E+01	12.964	64.822
5	20	100	99	2	4.7368	1.16E+01	15.263	76.316
5	20	100	99	3	2.9698	7.43E+00	17.030	85.151
10	20	100	99	1	ND	ND	ND	ND
10	20	100	99	2	ND	ND	ND	ND
10	20	100	99	3	ND	ND	ND	ND
5	30	100	100	1	-0.2408	2.37E+01	30.241	100.803
5	30	100	100	2	-1.5554	7.24E+00	31.555	105.185
5	30	100	100	3	1.9693	3.79E+01	28.031	93.436
10	30	100	100	1	ND	ND	ND	ND
10	30	100	100	2	ND	ND	ND	ND
10	30	100	100	3	ND	ND	ND	ND

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BIOGRAPHICAL SKETCH

Alexandra Guibord Rozin was born in New York City and grew up on Cape Cod. After attending local schools with her older sister and triplet brothers until the age of 17, she sought warmer weather and enrolled at New College in Sarasota, Florida, studying biology and environmental science. She ran through their biology courses in two years and spent a year at the University of Guam, where she came to appreciate arduous fieldwork, ecosystem science from a systems perspective, and the pleasure and pain of failed experiment (embracing the reality that both are part of the scientific process). Upon returning to the United States, Alexandra transferred to the University of Florida where she completed her undergraduate education in the Soil and Water Science Department. She had the opportunity to work with Drs. Todd Osborne and Rex Ellis on research projects spanning peninsular Florida. Long field days in the Everglades and the Florida Keys motivated her to complete her Master's degree in the same department under Dr. Mark Clark. After a brief vacation studying Gelisols in the arctic, Alexandra traded in her field shoes for a lab coat, rounding out her scientific education. The results of that time are presented on the pages of this thesis. After graduation, Alexandra will return to per passion of arduous soil science fieldwork as a doctoral student working on the Reynolds Creek Critical Zone Observatory at Idaho State University under the advisement of Dr. Kathleen Lohse.