

ABSTRACT

BELENKY, CYRUS NICHOLAS. The Effect of Stream Restoration on Water Quality and Quantity in the Coastal Plain of North Carolina (Under the direction of Dr. Francois Birgand)

Approximately \$1 billion are spent on stream and river restoration annually in North America, with little consensus on their effect on water quality or quantity. The absence of comprehensive or suitable monitoring methods could explain this lack of agreement. Current monitoring relies on infrequent sampling (e.g. every six months), and an uncertainty range that can equal or exceed the expected water quality benefits, making water quality changes undetectable, leading to unreliable conclusions about restoration effects. Therefore, we hypothesize that it is possible to reduce uncertainty of cumulative loads, at desirable levels for detection, by increasing sampling frequency from every six months to every 15 minutes. State-of-the-art, in-situ, ultraviolet-visible (UV-Vis) spectrophotometers collected absorbance data for nitrate, total phosphorus, total suspended solids, and dissolved organic carbon. This monitoring method was conducted at a 2.4 km long restored stream near Goldsboro NC. Flow and concentration measurements were collected before, during and after restoration at three stations, along the restored reach. Water quality and quantity data collected post-restoration were compared to data collected prior to restoration to assess the magnitude and direction of any change. As the restoration matured, seasonal patterns and long-term changes were quantified and used to improve practices for restoration and restoration monitoring.

© Copyright 2018 by Cyrus Nicholas Belenky

All Rights Reserved

The Effect of Stream Restoration on Water Quality and Quantity in
the Coastal Plain of North Carolina

by
Cyrus Nicholas Belenky

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

Biological and Agricultural Engineering

Raleigh, North Carolina

2018

APPROVED BY:

Dr. François Birgand
Committee Chair

Dr. Barbara Doll

Dr. Theodore Shear

BIOGRAPHY

Cyrus Nicholas Belenky was born 29 June 1993 to Gregory and Nicole Belenky. He grew up in Kensington, Maryland with his siblings, Nadya Belenky and Lucas Belenky. Cyrus attended The German School of Washington D.C., from K-12, graduating with both an American high school diploma and the German Abitur. He was always engaged in the outdoors, an avid boy scout and eventually also an avid Eagle Scout. He spent his summers close to or on the water, and developed an insatiable need to sail.

Cyrus attended North Carolina State University for his undergraduate degree immediately after high school initially pursuing a degree in Mechanical Engineering but changing course to earn a B.S. in Biological and Agricultural Engineering. Following the completion of his undergraduate degree in December of 2015, Cyrus immediately left to sail the coast of Mexico. It was that January that Cyrus had a conversation with an enthusiastic sailor with a graduate degree in oceanography. This sailor convinced Cyrus to pursue his graduate studies sooner rather than later. The recent graduate immediately applied to pursue a Master of Science in Biological and Agricultural Engineering at North Carolina State University under the direction of Dr. François Birgand. During this time, Cyrus studied the changes in water quality that have taken place due to the stream restoration at the Claridge Tree Nursery. Afterwards, it will back out on the water for him.

ACKNOWLEDGMENTS

I would like to give special thanks to all those who helped me get where I am today.

First, I am incredibly thankful to my mother and father, Nicole and Gregory Belenky, as well as my siblings, Nadya Belenky and Lucas Belenky. Without you, I may have never gone down any of the paths that lead me to where I am now. You are my foundation.

Second, I would like to thank Dr. François Birgand. Without you, I would have never had the opportunity to work on a project as exciting as this. What I have learned in the past two years is more than merely stream restoration, biogeochemistry and experimental design. Thank you. In addition, I want to extend my thanks to Dr. Barbara Doll and Dr. Theodore Shear, for your interest and willingness to be a part of my masters committee and for the interesting courses you teach.

Thank you to Maia Fitzstevens, your interest in and support of my work during the past nine months has been unyielding. Thank you to Emily McCain and her parents Beth and Paul McCain, who are my family away from home. Thank you to all my friends here and abroad that have encouraged me over the last two years.

Thank you to all the faculty and staff of the Biological and Agricultural Engineering Department here at North Carolina State University. Thank you to Neil Bane, the sheriff of Weaver Labs, and his team in the research shop. Neil, I hope my antics with the department vehicles did not tire you out. Thank you to Katy Mazer, the best office mate I didn't know I could ask for.

Thank you to the North Carolina Department of Transportation for funding this research.

TABLE OF CONTENTS

LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER 1: The Effect of Stream Restoration on Water Quality and Quantity in the Coastal Plain of North Carolina using High-Frequency In-situ Spectrophotometry	1
1.1 Introduction.....	1
1.2 An Introduction to Stream Restoration Monitoring.....	2
Lack of Monitoring Consensus	2
1.3 Hypotheses and Goals.....	9
1.4 Methods	9
Site Description.....	9
Station Selection & Infrastructure	11
Flow Calculations	16
High Frequency Water Quality Measurements and Water Sampling.....	18
Discrete Water Sampling for Establishing Water Quality Rating Curves	18
In-situ Spectrophotometer Installation and Maintenance	19
Monitoring Designs	21
Monitoring Designs used by Lin (2017) (v1.0)	21
Initial post-restoration system: Low Elevation Boxes, Spectrophotometer in Box (v2.0)	21
Low Elevation Boxes, Spectrophotometer in Stream (v2.1)	22
High Elevation Boxes, Spectrophotometer in Stream (v2.2).....	22
Data Collection and Site Maintenance.....	23
Lab Analysis	24
Degradation Study	25
Method to Calculate Concentrations from Absorbance Data	25
Calculating Nutrient Loading, Cumulative Loads and Cumulative Volumes	26
Data Quality Assurance	26
Flow Data.....	26
Spectral Data.....	27
1.5 Results and Discussion	32
Creating Index Velocity Ratings to Calculate Flow	29
Degradation Study Results.....	31
Discrete Sample Summary.....	32
PLSR Analysis and Summary.....	33
Continuity of Flow across Monitoring Periods.....	36
Change in Flow-weighted Concentrations Entering at CLUP.....	40
Change in Relative Cumulative DOC and Nitrate Loadings	41
Change in Cumulative DOC and Nitrate Loading at CLMD Relative to CLUP.....	42
Change in Cumulative DOC and Nitrate Loading at CLDN Relative to CLUP	43
Change in Total Volumes and Loads Pre- and Post-Restoration.....	44
Discussion of Possible Reasons for Apparent Relative Loading Changes between Stations.....	49
Major Visible Physical Effects of the Restoration.....	52
Metrics for Crediting the Restoration for the Measured Effects.....	54

Hypothetical DOC and Nitrate Loading had Pre-Restoration Relationships held true ...	54
CLDN/CLUP DOC Relationship Gives Clues to the Restoration Influencing	
Nutrient Dynamics	55
Nitrate Treatment within the Reach Relative to Stream and Flood Prone Area	57
1.6 Conclusions.....	60
1.7 Considerations for Future Work	61
Basic inlet/outlet sampling for UT1 and UT2.....	61
Hurricane and Event Sampling	61
1.8 References.....	63
Appendices.....	66
Appendix A: PLSR Calibration Plots	67
Appendix B: DOC and Nitrate Time Series Chemographs and Hydrographs.....	81
Appendix C: Site Visit Checklists and Datasheets	84
Appendix D: Data Processing Flow Chart.....	86

LIST OF TABLES

Table 1.	Environmental impacts of R-2554 and the required mitigations (NUE, 2011).....	1
Table 2.	Local land use/land cover and soil types surrounding the restoration (USGS, 2011). Watershed areas are additive from station to station.	11
Table 3.	Pre- and post-restoration channel characteristics (NEU, 2011).	13
Table 4.	Sampling Scheme Summary.	26
Table 5.	Analyte and EPA methods used by the EAL (Dr. Cong Tu, Personal Communication).....	28
Table 6.	Comparison of the correction factors derived from the index velocity ratings from Pre- and Post-Restoration.	32
Table 7.	Results of the paired T-test used to test for degradation between GS-A and GS-B for Spring/Summer (top) and Fall/Winter (bottom). Alpha = 0.05.	35
Table 8.	Summary of the discrete samples collected during the monitoring period.	36
Table 9.	Summary of all PLSR calibrations for all seasons, stations and parameters. * denotes NSE values that are unsatisfactory.....	39
Table 10.	Summary of PLSR calibration for TSS for all three stations (CLUP, CLMD, CLDN) using the entire monitoring period. * denotes NSE values that are unsatisfactory.....	40
Table 11.	Cumulative flow slopes pre-/post-restoration (* post 18-01-2015 data only).....	43
Table 12.	Relative and measured values for all parameters pre-/post-restoration and percent changes (* post 18-01-2015 data only).....	50
Table 13.	Annual mass of DOC and NO ₃ exported post-restoration compared to annual masses predicted using equations 3-6 in kg/yr.....	60
Table 14.	Stream properties used to calculate nutrient reduction metrics (NEU, 2011).....	63
Table 15.	Normalized apparent restoration effect in mg/m ² /day for DOC and NO ₃ and the percentage of total change in NO ₃ and percentage of total area corresponding to each change (*per m ² of floodprone area includes the approximate areas of UT1 and UT2.	64

LIST OF FIGURES

Figure 1.	Monitoring timeline, showing the periods for which continuous data was collected.	2
Figure 2.	Temporal resolution comparison for electrical conductivity relative to flow (Kirchner et al., 2004).	5
Figure 3.	Hypothetical double mass curves. Projected pre-restoration double mass curve (blue), post-restoration double mass curve (green) and the restoration effect.	7
Figure 4.	Top hypothetical double mass curves and cumulative load error ranges using conventional sampling techniques (A) and bottom high frequency sampling (B). Projected pre-restoration double mass curve (blue) and post-restoration double mass curve (green).	9
Figure 5.	Watershed map with subwatersheds (SW) that drain into each monitoring station. Restored canal (purple), restored tributaries UT1 and UT2 (orange) and the unrestored tributary UT3. Modified from Lin (2017).	12
Figure 6.	Cross-section of a Priority 2 Restoration of a Stream, original surfaces shown as the dotted line (Doll et al., 2003). Dimensions are not to scale.	14
Figure 7.	Left, The Canal pre-restoration. Sinuosity of 1 and a disconnected floodplain. Right, The Canal post-restoration. Sinuosity of 1.25 and a connected floodplain. .	14
Figure 8.	Plan view of the stream reach M1, UT1 and UT2. Monitoring stations CLUP (green), CLMD (yellow) and CLDN (red).	15
Figure 9.	CLUP station with raised platform.	16
Figure 10.	CLMD station with raised platform.	16
Figure 11.	CLDN station with raised platform.	17
Figure 12.	Image of flume and the floodplain curtain at CLMD during construction.	18
Figure 13.	Schematic of monitoring system used in Lin et al., (2017).	22
Figure 14.	Left, looking upstream from HWY-70 shows standing water retained on the floodplain for up to a week following heavy rains on April 24 th & 25 th . Photo taken April 28th; Right, looking downstream at HWY-70 shows the same section in its normal state on May 11th after flooding subsided.	25
Figure 15.	Raw Sensor Velocity versus Mean Channel Velocity (a) CLUP; (b) CLMD; (c) CLDN (top to bottom).	34

Figure 16.	Regression relationships between measure DOC (left column) and nitrate (right column) from discrete sampling and PLSR predictions; CLUP, CLMD and CLDN from top to bottom.	37
Figure 17.	Timeline of drought conditions in Wayne County, NC from 2014-2018. 6-month monitoring periods in green. (Dark gray = abnormally dry, light gray= moderate drought).....	41
Figure 18.	Cumulative Volume CLMD (blue) & CLDN (red) (mm) vs. Cumulative Volume CLUP without Little River events (dashed) and all post-restoration data (solid).	44
Figure 19.	Cumulative Volume CLMD (blue) & CLDN (red) (mm) vs. Cumulative Volume CLUP (mm using data from Lin (2017) from 18-01-2015 onward (dashed), all post-restoration data (solid).....	45
Figure 20.	Flow-weighted DOC (brown) and nitrate (pink) concentrations entering CLUP using data from Lin (2017) (dashed) and data collected by Belenky (solid).....	46
Figure 21.	Seepage entering the restoration through the daylighting.....	48
Figure 22.	Cumulative DOC CLMD (solid) & CLDN (dashed) (kg/ha) vs. Cumulative DOC CLUP (kg/ha).	51
Figure 23.	Cumulative DOC CLMD (solid) & CLDN (dashed) (kg/ha) vs. Cumulative DOC CLUP (kg/ha) using data from Lin (2017) from 18-01-2015 onward.....	52
Figure 24.	Cumulative nitrate CLMD (solid) & CLDN (dashed) (kg/ha) vs. cumulative nitrate CLUP (kg/ha) and one-to-one line (long dashed).....	53
Figure 25.	Cumulative nitrate CLMD (solid) & CLDN (dashed) (kg/ha) vs. cumulative nitrate CLUP (kg/ha) using data from Lin (2017) from 18-01-2015 onward and one-to-one line (long dashed).	54
Figure 26.	Diagram from Findlay (1994) demonstrating the exchange of water with the hyporheic zone in all three dimensions.....	57
Figure 27.	Alligatorweed covering the channel during the summer.	58
Figure 28.	Post-restoration DOC CLDN vs CLUP in three distinct phases; Phase I (blue), Phase II (orange), Phase III (yellow).	62
Figure A1.	Regression relationships between measured nitrate concentrations from discrete sampling and predicted nitrate concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).....	73

Figure A2.	Regression relationships between measured DOC concentrations from discrete sampling and predicted DOC concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).....	75
Figure A3.	Regression relationships between measured ammonium concentrations from discrete sampling and predicted ammonium concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).....	77
Figure A4.	Regression relationships between measured phosphate concentrations from discrete sampling and predicted phosphate concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).....	79
Figure A5.	Regression relationships between measured total kjeldahl nitrogen concentrations from discrete sampling and predicted total kjeldahl nitrogen concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).	81
Figure A6.	Regression relationships between measured total phosphorus concentrations from discrete sampling and predicted total phosphorus concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).	83
Figure A7.	Regression relationships between measured total phosphorus concentrations from discrete sampling and predicted total phosphorus concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).	85
Figure B1.	CLUP flowrate [L/s] (blue) and instantaneous DOC concentration [mg/L] (orange).....	87
Figure B2.	CLUP flowrate [L/s] (blue) and instantaneous nitrate concentration [mg/L] (orange).....	87
Figure B3.	CLMD flowrate [L/s] (blue) and instantaneous DOC concentration [mg/L] (orange).....	88
Figure B4.	CLMD flowrate [L/s] (blue) and instantaneous nitrate concentration [mg/L] (orange).....	88
Figure B5.	CLDN flowrate [L/s] (blue) and instantaneous DOC concentration [mg/L] (orange).....	89

Figure B6. CLMD flowrate [L/s] (blue) and instantaneous nitrate concentration [mg/L] (orange).....	89
Figure C1. Fillable data collection sheets used during each field visit to ensure consistent data collection.	90
Figure D1. Data Processing and PLSR flowchart created to visualize the method.	92
Figure E 1. Cumulative volume CLMD (solid) & CLDN (dashed) (mm) vs. cumulative volume CLUP (mm) and one-to-one line (long dashed). Events where the Little River influenced water quality in The Canal are circled in orange.	93
Figure E 2. Cumulative DOC CLMD (solid) & CLDN (dashed) (kg/ha) vs. cumulative DOC CLUP (kg/ha) and one-to-one line (long dashed). Events where the Little River influenced water quality in The Canal are circled in orange.	94
Figure E 3. Cumulative nitrate CLMD (solid) & CLDN (dashed) (kg/ha) vs. cumulative nitrate CLUP (kg/ha) and one-to-one line (long dashed). Events where the Little River influenced water quality in The Canal are circled in orange.	95

CHAPTER 1: The Effect of Stream Restoration on Water Quality and Quantity in the Coastal Plain of North Carolina using High-Frequency In-situ Spectrophotometry

1.1 Introduction

In 2011, the North Carolina Department of Transportation (NCDOT) began construction on Transportation Improvement Program R-2554 U.S. Highway 70 Goldsboro Bypass (TIP R-2554). As part of the planning process for R-2554, NCDOT was required by Section 404 of the Clean Water Act (CWA) to follow a three-step plan to avoid, minimize and mitigate for impacts to aquatic systems (EPA, 2008). NCDOT distributed the required compensatory mitigation across nine mitigation sites. The largest of these sites was the restoration of ‘The Canal’ at the North Carolina Forestry Service (NCFS) Claridge Nursery located in Section A of R-2554 (NEU, 2011). Table 1 lists the unavoidable impacts, which required compensatory mitigation at the NCFS Claridge Nursery.

Table 1. Environmental impacts of R-2554 and the required mitigations (NUE, 2011).

	Impacted by R-2554	Required by mitigation	Mitigated at Claridge
Streams (feet/m)	15,125 / 4,610.1	15,263 / 4652.2	10,397 / 3,169 (68%)
Wetlands (acres/hectare)	27.16 / 10.99	29.36 / 11.88	-
Riparian Buffer (ft ² /hectare)	1,358,482 / 12.6	1,453,479 / 13.5	994,657 / 9.2 (68%)

The goal of this study, directed by Dr. Birgand from the department of Biological and Agricultural Engineering at NC State University, was to answer questions posed by NC DOT, which include: (1) What is the magnitude of the water quality benefit of a stream restoration in rural North Carolina and (2) can one derive monitoring guidelines for future restoration projects? The research team used state of the art continuous water quality monitoring methods before,

during, and after restoration to capture the bulk water quality effect of the restoration in this Claridge stream. To determine the restoration effect, changes in cumulative loads at two treatment stations (middle and end of the restoration) were quantified and compared to the cumulative loads entering the treatment station (the beginning of the restoration), during both the pre- and post-restoration. The study uses the data collected by Chiao-Wen Lin (Lin, 2017) from 2013 until 2015 and the data collected during the first post-restoration year, 2017 until 2018. A full breakdown of the monitoring timeline is provided in Figure 1.

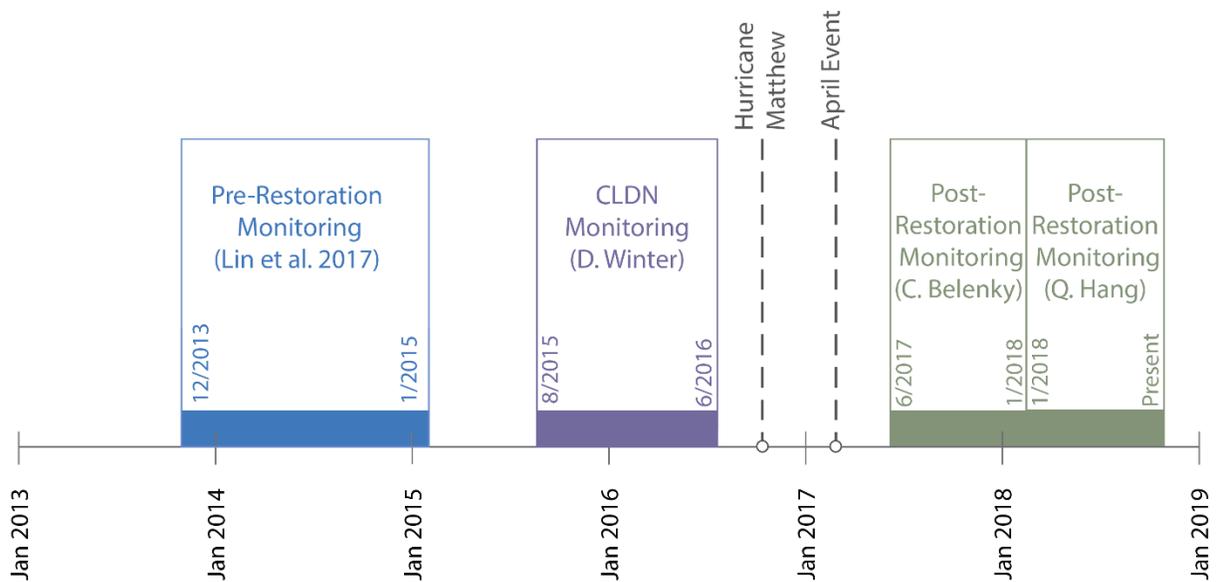


Figure 1. Monitoring timeline, showing the periods for which continuous data was collected.

1.2 An Introduction to Stream Restoration Monitoring

Lack of Monitoring Consensus

Stream restoration is a growing field around the world. In the United States, stream restoration and environmental mitigation projects cost roughly \$15 billion between 1990 and 2005 (Bernhardt et al., 2005). This equates to roughly \$1 billion spent annually on restoration and mitigation. Bernhardt et al. (2005) conservatively estimated that the of annual restoration

spending and the actual cost of restorations since 2005 has likely exceeded \$12 billion (\$1 billion/year over 12 years) (Kenney et al., 2012). At the time of the Bernhardt et al. (2005) publication, the number of projects and restoration related articles were already on the rise, suggesting that yearly expenditures for restorations are higher now than initially reported. (Bernhardt et al., 2005; Palmer, Allan, Meyer, & Bernhardt, 2007). Since 2005, the number of restoration projects and scientific papers published has continued to increase, supporting this assumption. The number of scientific papers published on restoration increased from 17 in 2005 to at least 35 in 2012 (Wortley, Hero, & Howes, 2013). Despite large expenditures in mitigation and restoration, there is little consensus on the efficacy of restoration, due to a lack of data, insufficient data, or poor-quality data (Bernhardt et al., 2005; Palmer et al., 2007). Data collected on roughly 37,000 river and stream restorations by the National River Restoration Science Synthesis (NRRSS) showed that a fifth of compiled projects listed no objectives for the restoration. Downs and Kondolf (2002) emphasize that it cannot be taken for granted that restoration projects are inherently “good” or positive. Only one tenth of projects surveyed, conducted monitoring or assessment, with the majority not intending to analyze the collected data (Bernhardt et al., 2005). Prior to this project, studies analyzed the effect on water quality by comparing the restored reach to a nearby reference reach (Bosch & Hewlett, 1982; Colangelo, 2014; Howson, Robson, & Mitchell, 2009). While this method is less time intensive, only requiring monitoring of the restored and reference reach post-restoration, it does not compare the state of water quality pre-restoration to post-restoration. Predetermined restoration goals and adequate pre- and post-restoration data are required to determine the success of a restoration. Without pre- and post- restoration monitoring and comparing between the two states, it becomes

difficult to reliably quantify the restorations effect on the area (Morandi, Piégay, Lamouroux, & Vaudor, 2014).

In addition to non-existent monitoring plans, many projects implementing monitoring did so poorly. The same study concluded that projects with the worst monitoring methods reported the highest success rates, showing that current techniques improperly quantify the restoration effect (Morandi et al., 2014). Contemporary water quality monitoring for environmental mitigation in North Carolina requires only infrequent sampling of surface waters. The U.S. Army Corps of Engineers (USACE), Wilmington District's guidelines require sample collection at six-month intervals. The sampling interval for water quality is infrequent because the USACE does not evaluate mitigation success based on water quality data (USACE & EPA, n.d.). Figure 2 shows a comparison between measured electrical conductivity at monthly, weekly, daily and hourly intervals. The results showed that monthly and even weekly sampling failed to capture detailed system behavior, while daily and hourly intervals captured events of shorter duration and showed a more detailed picture of the processes taking place in the body of water (Kirchner, Feng, Neal, & Robson, 2004).

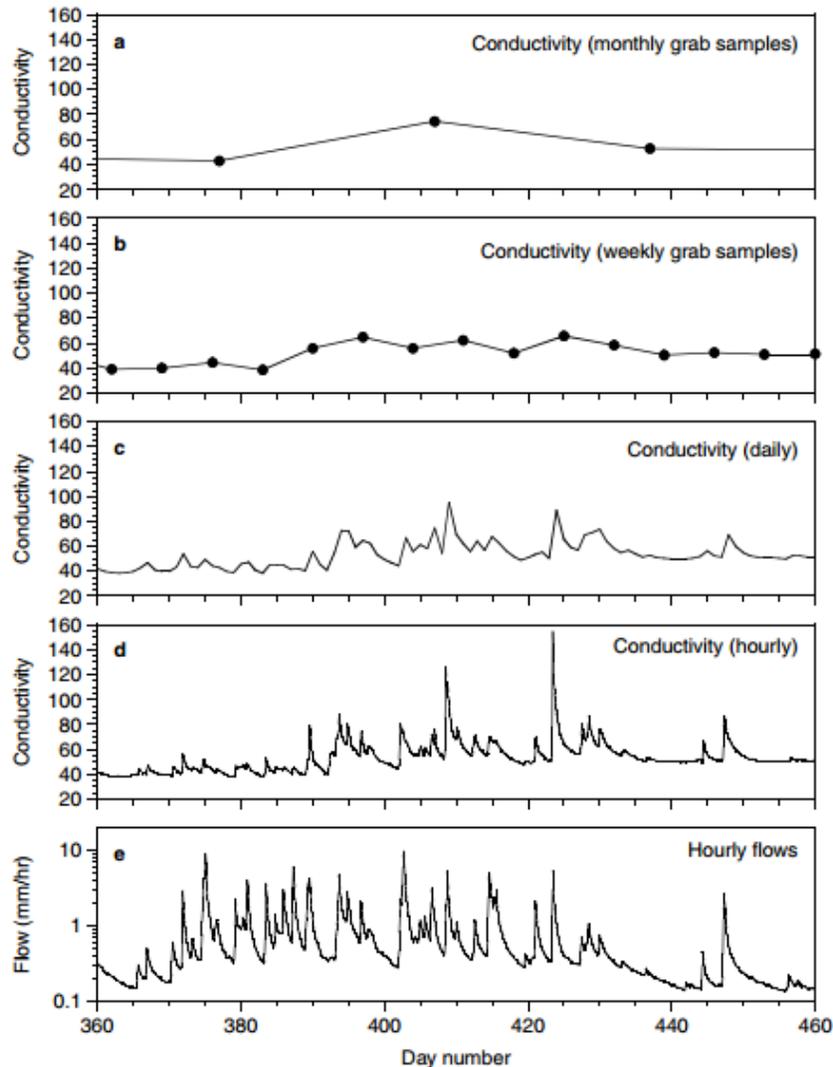


Figure 2. Temporal resolution comparison for electrical conductivity relative to flow (Kirchner et al., 2004).

The low temporal resolution of such monitoring schemes provides an imprecise representation of system behavior. Additional studies have shown that the error associated with these contemporary monitoring methods can be several times greater than the expected restoration effect (F Birgand, Appelboom, Chescheir, & Skaggs, 2011). From a mathematical perspective, Birgand et al. (2017) and Howden et al. (2018) have suggested that these discrete concentration indicators, used in contemporary water quality monitoring, are equivalent to ‘derivative’ indicators, which are subject to high coefficients of variation. Unless their full

variability is taken into account, concentrations are inherently not robust indicators for water quality (F. Birgand, Howden, Burt, & Worrall, 2017; Howden, Birgand, Burt, & Worrall, 2018). ‘Integrative’ indicators that (mathematically) integrate or cumulate derivative indicators are inherently more robust to detect trends.

We have therefore proposed to use cumulative loads as robust indicators, i.e. integrating over time both concentration and velocity data measured at high frequency. 15-minutes has been found to be frequent enough to capture the temporal variations occurring within the reach (Lin, 2017). Sampling at high frequency has already shown potential to track pollutant patterns not possible with infrequent sampling. Multiple studies have used in-situ spectrometers to collect, 30-minute interval samples with results that underscore the need for high temporal resolution data. Morandi et al., (2014) suggest that increased number of samples collected with a high sampling frequency produces an increase in statistical power to detect ecological changes in mitigation and restoration projects (Morandi et al., 2014). We suggest that a three-fold shift in monitoring practices is required to determine, with increased certainty, the effect of stream restoration on water quality.

The three changes are to:

1. conduct restoration monitoring;
2. monitor pre- and post-restoration; and
3. monitor at high frequency.

Three monitoring stations were constructed, along the unrestored reach after the restoration was completed, at the beginning (CLUP), the middle (CLMD), and at the end (CLDN). The three stations along the reach monitored water quality both pre- and post-restoration. CLUP is the control for the watershed study while CLMD and CLDN are ‘treatment

stations'. The method used to detect the bulk water quality effect of the stream restoration of The Canal uses an approach analogous to a paired-watershed study – a method often applied in hydrology (Andréassian, Parent, & Michel, 2003; Bosch & Hewlett, 1982; Hornbeck, Adams, Corbett, Verry, & Lynch, 1993; Stednick, 1996). Instead of pairing spatially separate watersheds, this study paired the reference monitoring station with the two treatment stations. We compared the cumulative loads passing through each station to the cumulative load passing through the reference station. The degree of inflection of the double mass curves of the post-restoration curve from the pre-restoration curve should be indicative of the restorations effect on bulk water quality (Figure 3).

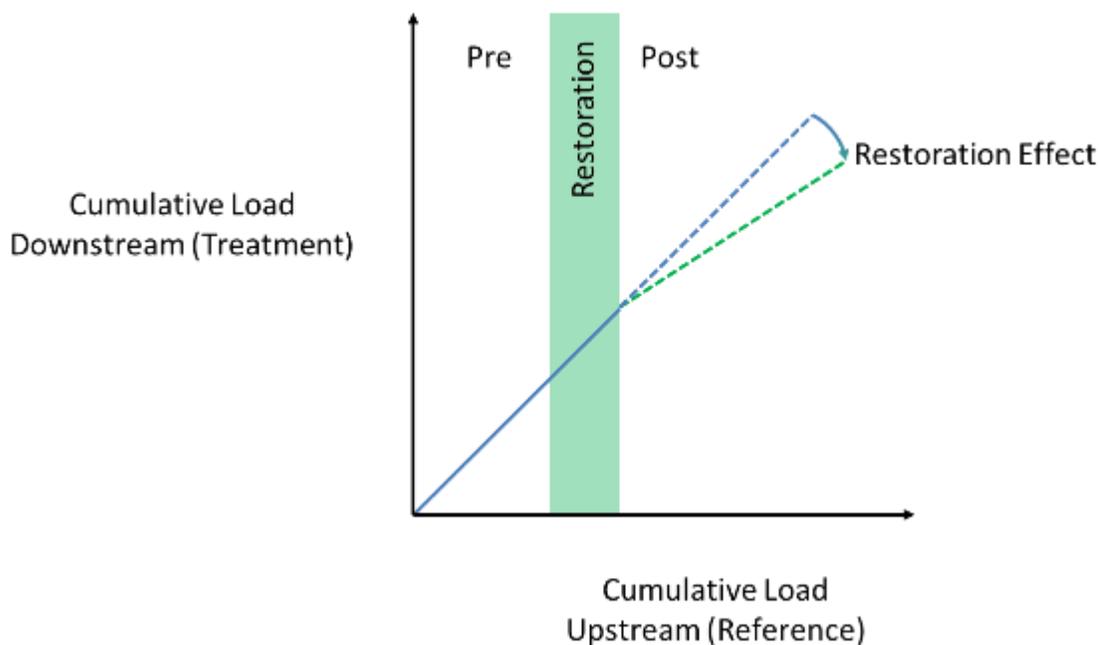


Figure 3. Hypothetical double mass curves. Projected pre-restoration double mass curve (blue), post-restoration double mass curve (green) and the restoration effect.

However, this method relies on two other hypotheses. First, that nutrient additions corresponding to the nested watersheds between stations do not change significantly between the pre- and post-restoration periods. Secondly, that the magnitude of the bulk water quality effect has to be several times larger than the monitoring uncertainties. Lin (2017) has shown that

conventional sampling methods can generate errors in annual nitrate loads of $\pm 30\%$ for nitrate for monthly sampling (Lin, 2017).

Taking these into account when considering the cumulative loads at CLUP and CLDN (Figure 4A) for example, we can draw the “angles” of uncertainty corresponding to annual loads $\pm 30\%$. However, to detect a water quality effect the uncertainty “angles” have to be several-fold smaller than the estimated effect (Figure 4B). Uncertainty “angles” smaller than the measured effect are reasonable, as Lin et al. (2017) found that uncertainties for some parameters to be as low as $\pm 3\%$ for nitrate for example (Lin, 2017). To reduce the uncertainty in water quality monitoring, it is essential that we measure flow and pollutant concentration as accurately as possible. To do so we have opted for high frequency Doppler-based flow measurements in constructed trapezoidal wooden flumes, and high-frequency concentration measurements using in-situ spectrophotometers.

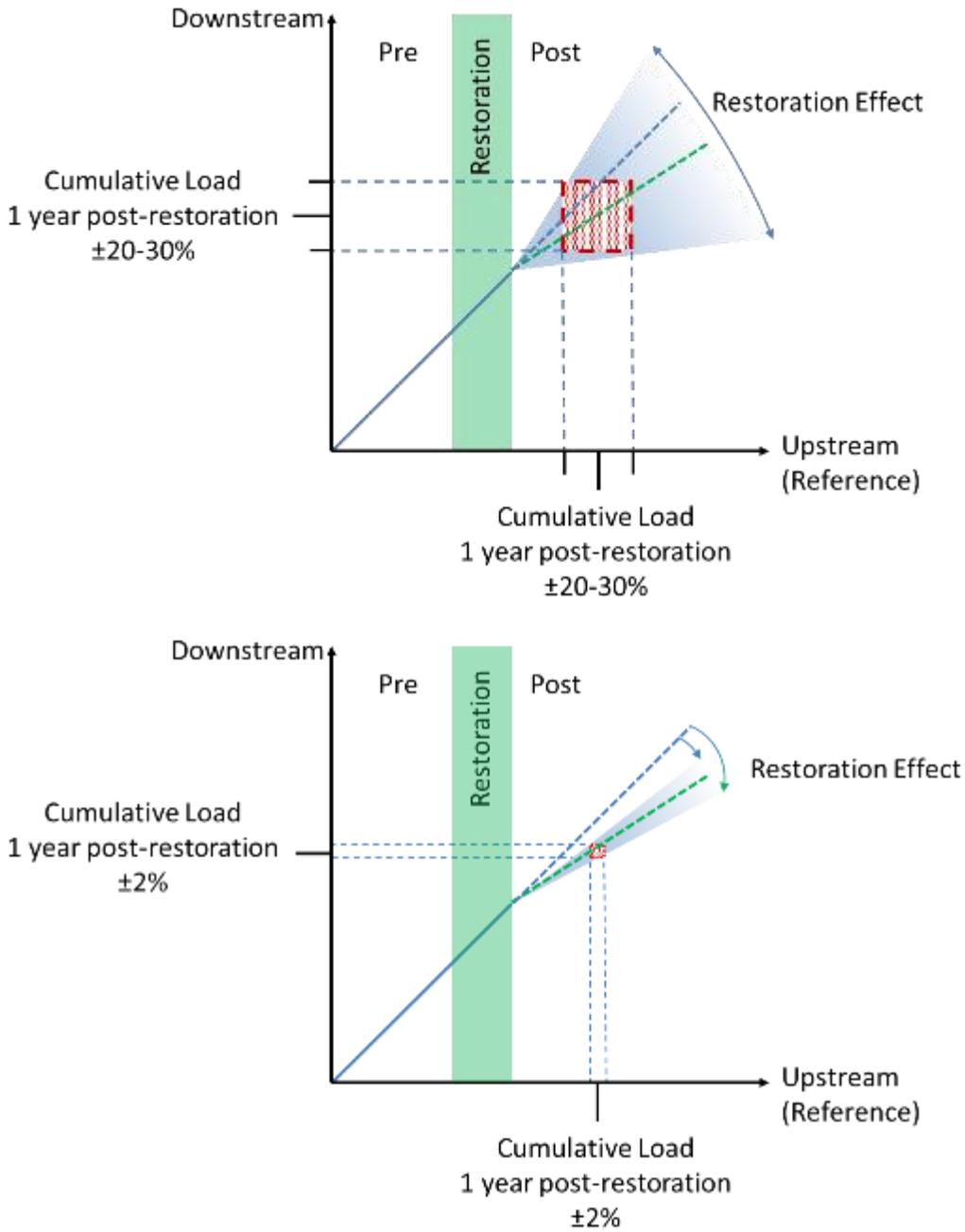


Figure 4. Top hypothetical double mass curves and cumulative load error ranges using conventional sampling techniques (A) and bottom high frequency sampling (B). Projected pre-restoration double mass curve (blue) and post-restoration double mass curve (green).

1.3 Hypotheses and Goals

We hypothesize the following:

- High frequency in-situ Ultraviolet-Visible (UV-Vis) spectrophotometry, can be used to effectively monitor the concentrations of ammonium, total kjeldahl nitrogen, total suspended solids, dissolved organic carbon, nitrate/nitrite, total phosphorous, phosphate in a restored stream.
- High frequency velocity and flow data can be used to construct double mass curves post-restoration using the concentration calibration method established during pre-restoration monitoring.
- Cumulative volumes and loads of DOC and nitrate can be used to quantify the restoration effect from pre- to post-restoration.
- Treatment effect of the restoration per unit length of stream can be quantified.

The objectives for this study are:

- Collect high frequency flow and water quality data post-restoration;
- Improve monitoring systems in order to reduce gaps in high frequency sampling;
and
- Quantify the restoration effect using double mass curves from data collected pre- and post-restoration for DOC and nitrate through the reach.

1.4 Methods

Site Description

As mentioned previously, the location chosen by the NCDOT for the compensatory mitigation of TIP R-2554 is on the NCFS Claridge Tree Nursery. The Claridge nursery is in Wayne County, North Carolina, just west of the city of Goldsboro. One of the prominent features

at Claridge is The Canal, a 2.2 km agricultural ditch that ran approximately north to south through the nursery. The three dominant land uses for The Canal’s watershed are cropland (57%), forest (14%) and developed land (10%), with the dominant soil types being B (63%), A (20%), C (11%) and D (6%). According to the 2001 National Land Cover Database (NLCD), (Table 2). Over the course of 12 months beginning in the fall of 2015, a private environmental consulting firm under the direction of the NCDOT restored The Canal. The restoration consisted of three parts, the restoration of The Canal from a Rosgen type F stream to a type E according to the Rogen Stream Classification System and two unnamed tributaries (UT1 and UT2) (Rosgen, 1994). These sections are 2,652, 230 and 541 meters long, respectively (NEU, 2011). A third unnamed tributary (UT3) flowed into the reach between CLMD and CLDN but was not altered as part of the restoration (Figure 5).

Table 2. Local land use/land cover and soil types surrounding the restoration (USGS, 2011). Watershed areas are additive from station to station.

Station	CLUP (SW I)		CLMD (SW I+II)		CLDN (SW I+II+III)	
Watershed Area (ha)	236		414		573	
	Percentage of Area (%)	Area (ha)	Percentage of Area (%)	Area (ha)	Percentage of Area (%)	Area (ha)
Classification of Vegetation Cover and Land Use						
Cultivated Crops and Hay	57	134	57	237	57	328
Forest	12	28	16	66	14	78
Developed land	5	11	5	19	10	55
Wetland	11	24	8	34	7	38
Impervious Area	1	2	1	4	3	15
Shrub	2	6	1	6	1	6
Other	12	30	12	48	9	53
Hydrologic soil Classification						
Group B	57	134	68	279	63	362
Group A	23	55	18	74	20	112
Group C	13	30	10	42	11	61
Group D	7	17	4	17	6	35

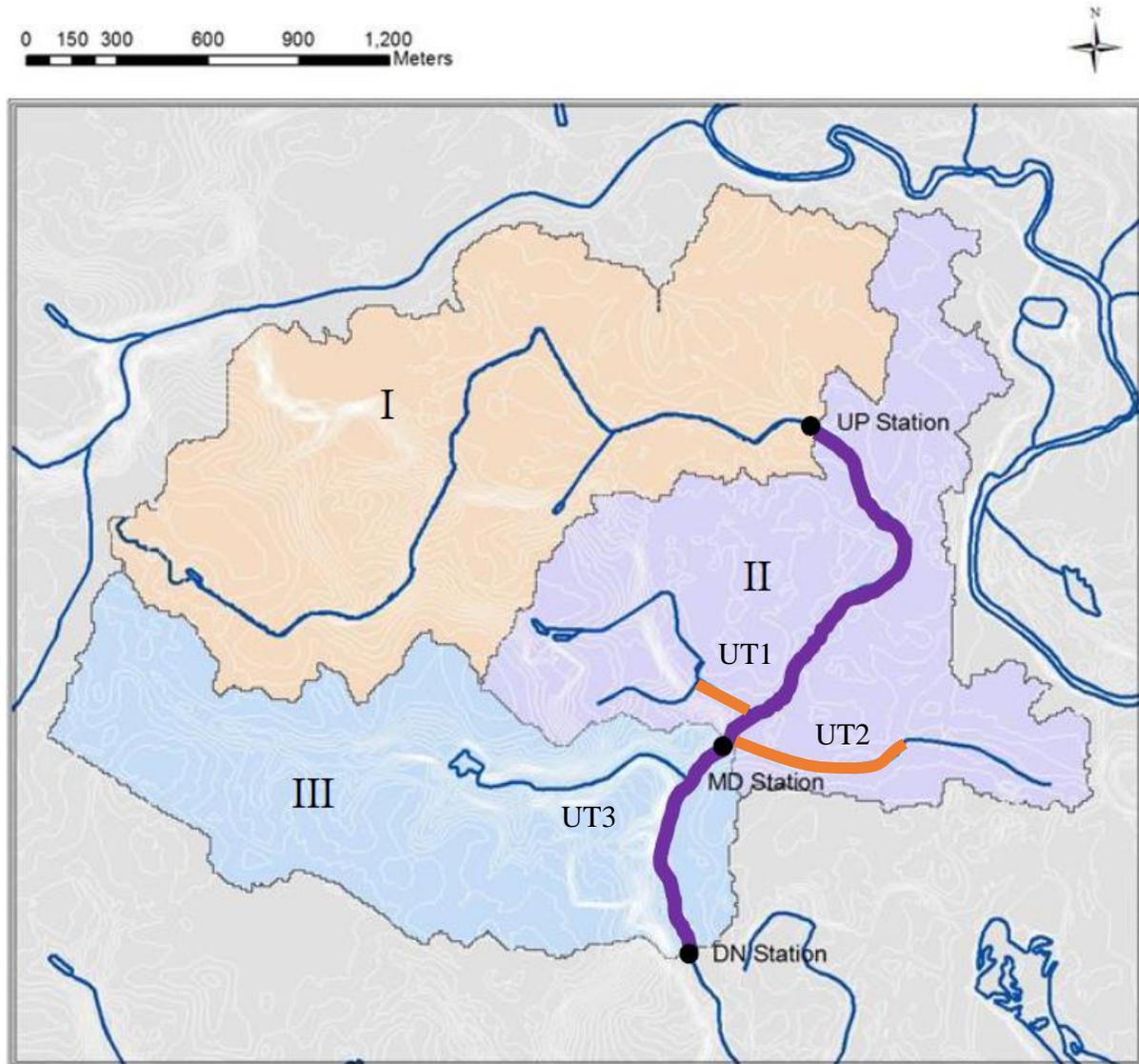


Figure 5. Watershed map with subwatersheds (SW) that drain into each monitoring station. Restored canal (purple), restored tributaries UT1 and UT2 (orange) and the unrestored tributary UT3. Modified from Lin (2017).

The Canal underwent a priority 2 restoration (Figure 6), the surrounding terrace was excavated to create a new floodplain and a new meandering channel was added along the entire length (Doll et al., 2003). To create the new meandering channel and 19-meter-wide floodplain for Section M1, construction crews excavated the surface surrounding the agricultural ditch by a depth of approximately 2.5 meters. This process converted The Canal from a straight low gradient channel (Type F stream) to a sinuous low gradient channel with a connected floodplain

(Type E/C5) (NEU, 2011; Rosgen, 1994). The first two unnamed tributaries were similarly widened and lowered but were not given a meandering channel. Instead the tributaries were roughened and allowed to self-design into low gradient braided channels (Type DA5) (NEU, 2011; Rosgen, 1994).

Station Selection & Infrastructure

Once the restoration construction was completed (Figure 7), we established monitoring stations on site. Post-restoration monitoring of the canal used three sampling stations like those used during the pre-restoration phase. We followed the same approach as during pre-restoration, constructing trapezoidal wooden flumes in the channel taking care to keep the shape as close as possible to the channel geometry so as not to impede flow. Stations were in linear stream sections where downstream scour was less likely. The CLUP and CLDN stations were constructed close (10 – 15 m) to the beginning and end of the restored reach (M1). CLMD was constructed approximately 1,670 m downstream of CLUP, just downstream of the two unnamed tributaries (UT1, UT2) that flow into M1. Flow and concentration inputs from UT1 and UT2 were not monitored individually. Figure 8 indicates the locations of the monitoring stations along the reach.

Table 3. Pre- and post-restoration channel characteristics (NEU, 2011).

	Pre-Restoration		Post-Restoration	
		CLUP until Bridge #3	Bridge #3 until CLDN	All
Length (m)		975	1,225	2,652
Bankfull width (m) (m)		6	9	4
Bottom width (m)		3	4.5	1.7
Bankfull Depth (m)		1.75	2.5	0.5
Sinuosity		1	1	1.25

Priority 2 Restoration

New Stable Channel

Lower Floodplain

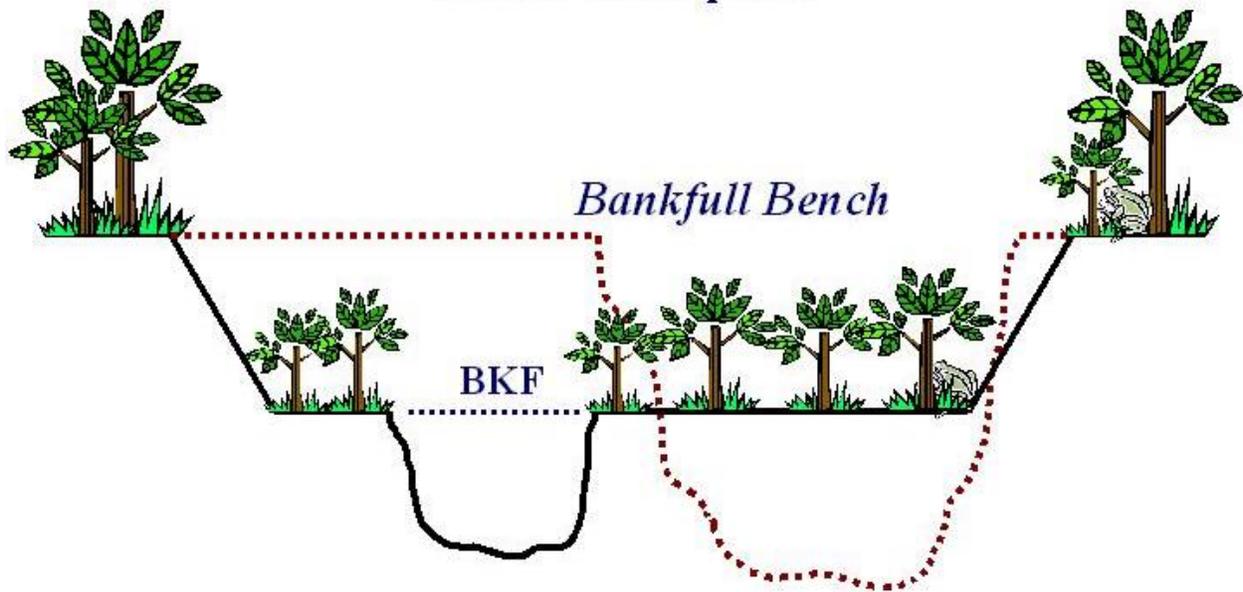


Figure 6. Cross-section of a Priority 2 Restoration of a Stream, original surfaces shown as the dotted line (Doll et al., 2003). Dimensions are not to scale.



Figure 7. Left, The Canal pre-restoration. Sinuosity of 1 and a disconnected floodplain. Right, The Canal post-restoration. Sinuosity of 1.25 and a connected floodplain.

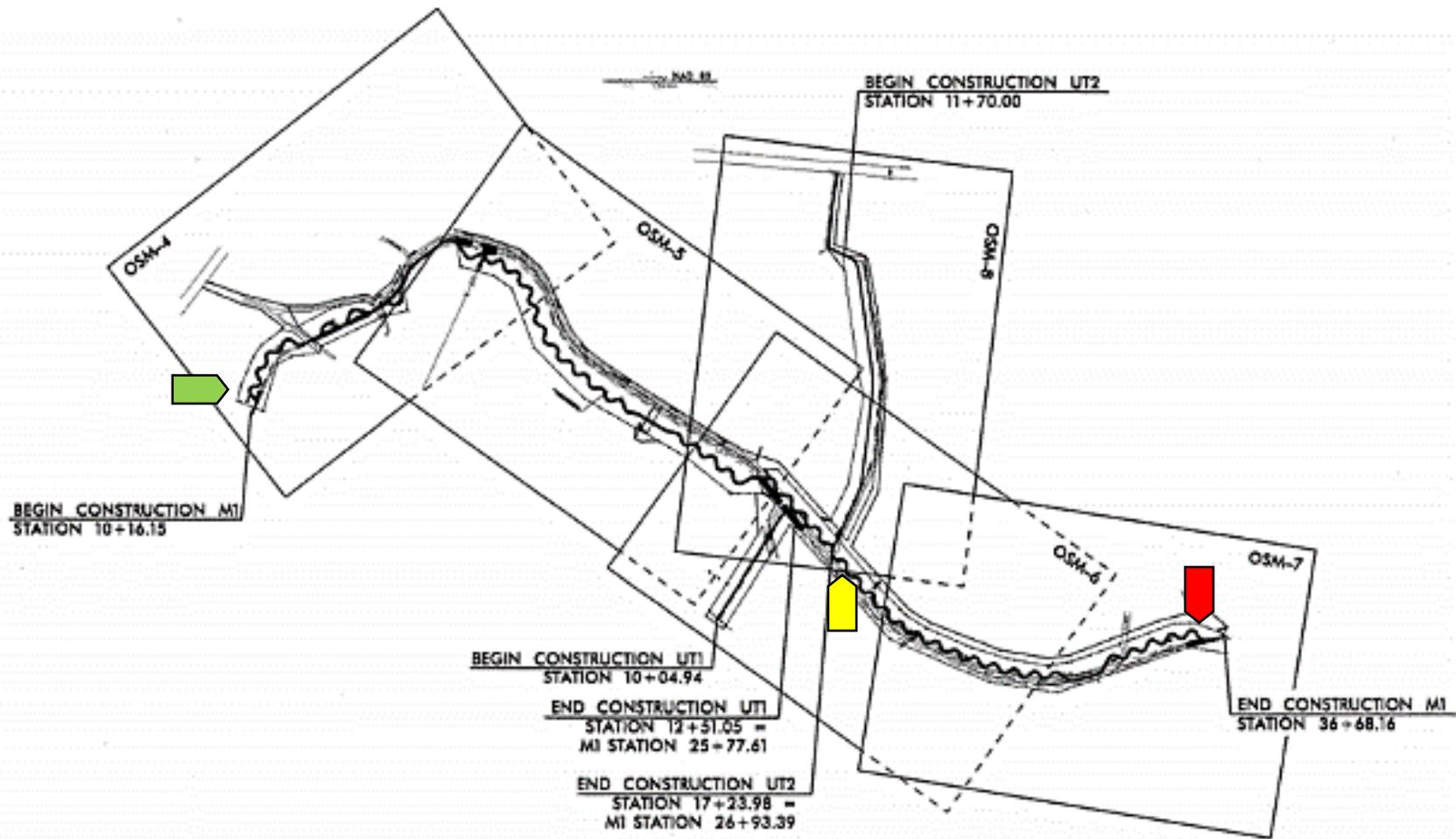


Figure 8. Plan view of the stream reach M1, UT1 and UT2. Monitoring stations CLUP (green), CLMD (yellow) and CLDN (red).



Figure 9. CLUP station with raised platform.



Figure 10. CLMD station with raised platform.



Figure 11. CLDN station with raised platform.

The flumes are used to create as laminar flow as possible in a wetted cross-section of precisely measurable area. The flumes were partially pre-fabricated prior to installation to ensure uniformity of construction. To limit sedimentation in the flume, the streambed was excavated to bring the bottom of the flume about 5cm above the channel bottom. Five-foot sections of rebar, set at an angle, were used to anchor the bottom of the flume to the streambed. The rebar was secured to the interior members of the base of the flume. To ensure that the flow rate through the flume was calculated as accurately as possible, all flow was routed through the flume. This included flow events where stage rose above bank full and inundated the floodplain. To restrict flow across the floodplain, a floodplain polypropylene curtain was erected across the floodplain (Figure 12). Extending from the upstream mouth of the flume, outward onto the floodplain terrace, the curtain funnels water from the floodplain through the flume. Held upright by wooden 2x4s driven into the floodplain and one foot of the curtain buried below the elevation of the floodplain to prevent water from flowing underneath the curtain and causing erosion. During

high or “flashy” rain events, it is expected that the floodplain curtain may be overtopped or knocked over.

Station installation began in August of 2016 and was due to finish by mid-October. However, on October 8th, 2016, Hurricane Matthew destroyed the only operational station at the time, resetting construction progress. All stations were completed in early 2017.



Figure 12. Image of flume and the floodplain curtain at CLMD during construction.

Flow Calculations

In lowland areas, and because of variable downstream control, the stage-discharge relationship tends to be unstable and may change during events and over time (François Birgand, Lellouche, & Appelboom, 2013). Consequently, the measurement of the stage alone to calculate flow is not reliable for our conditions. Therefore, we used acoustic Doppler velocity meters (ADVMS) installed in the flumes to measure water velocity and stage. The known channel geometry provided by the section reduces the uncertainty in determining discharge through the monitoring station (Robinson & Chamberlain, 1960). The ADVMS are mounted to the bottom of the downstream end of the flume, where flow is most laminar. The ADVMS also log stage and temperature in addition to measuring velocity through the section.

ADVMS send out bursts of ultrasonic sound beams in multiple directions through the water column. Particles traveling through the path of the beam reflect the sound back at the instrument, albeit with a frequency shift. This frequency shift is what the instrument uses to calculate the velocity of particles within the beam. The sound beams are directed left and right of center as well as fore and aft from the device (SonTek/YSI, 2011; SonTek, 2015). Lin (2017) has found that the center beams were more stable and used as index values to calculate flow (Lin, 2017). Measuring flow using the Doppler principle works best under laminar flow conditions, hence the importance of constructing the flumes in sections of the stream where flow was already somewhat laminar. Because storm events carried more particles from which the ultrasonic bursts could be reflected, these events provided especially smooth flow measurements. Measurements are less reliable during times of low velocity and high stage, where the amount of reflected sound from moving particles was relatively small and became blurred by noise from fish or wind ripples at the stream surface. Because of these considerations, velocity data was closely scrutinized and analyzed to smooth and remove outliers (see procedures in Data Quality Assurance).

The measured stage and the geometry of the trapezoidal flumes were used to determine the wetted cross-sectional area (A). Cross-sectional average velocities through each section were calculated using the ‘index velocity’ method at each station (F. Birgand et al., 2005; ISO 15769, 2010; Morlock, Nguyen, & Ross, 2002). A ‘velocity rating curve’ was derived from a linear regression between manual mean velocities and the sensor velocities for the same time-stamp. Cross-section average velocities (V) were calculated from manual gauging obtained during bi-weekly maintenance visits using the velocity area method (ISO 748, 1997). Manual measurements were collected using a portable flowmeter (Marsh-McBirney Inc., 1990). Flow

was calculated using the continuity equation product of the cross-section average velocity and the wetted cross-sectional area.

$$Q = V * A \quad \text{(Equation 1)}$$

High Frequency Water Quality Measurements and Water Sampling

Spectrophotometers were used at each monitoring station to collect light absorbance data of the water passing through each station. These spectrophotometers are capable of capturing absorbance values in the 220 to 742.5 nm wavelength range across a 5 mm path length. As with flow, absorbance values are used as index values or input to water quality or absorbance rating curves to calculate concentrations.

The spectrophotometers are capable of calculating concentrations from absorbance data for dissolved organic carbon (DOC), nitrate (NO_3^-) and turbidity. However, previous research has shown that it is possible to create superior rating curves on site, referred to as ‘local calibrations’, to correlate the absorbance values at different wavelengths to known pollutant concentrations. These local calibrations are suitable for Ammonium (NH_4^+), Total Kjeldahl Nitrogen (TKN), Total Suspended Solids (TSS), Total Phosphorus (TP), Phosphate (OPO_4), and salinity in addition to nitrate, DOC and turbidity (J R Etheridge et al., 2014). Light absorbance is correlated to known pollutant concentration with the use of a partial least square regression (PLSR) (J R Etheridge et al., 2014; Lepot et al., 2016; Lin, 2017). The sampling method used to collect the calibration data is discussed in the following sections.

Discrete Water Sampling for Establishing Water Quality Rating Curves

Discrete samplers are commonly used for concentration-based water quality studies. Using a discrete sampling scheme, an automated sampler can only collect as many discrete samples as it has bottles available before the bottles need to be changed. In this study, automated

samplers collected samples at 14-hour intervals, allowing 24 samples to be collected over a two-week period. Samples were transferred to a cooler during bi-weekly maintenance visits to the site and returned to Weaver Laboratories for analysis by the Environmental Analysis Laboratory (EAL). To create the best possible calibration for the spectrophotometers, it is best to obtain stratified concentration samples as well as samples stratified across the bi-weekly monitoring period (Lin et al., 2017). Stratification across time is beneficial when correcting for fouling of the spectrophotometer optics. Fouling of the optics was the results of either biological growth (algae or biofilms) forming on the lenses of the spectrophotometer or chemicals adhering to the lenses, both of which altered the absorbance measured by the spectrophotometer (Lin et al., 2017; J Randall Etheridge et al., 2013).

In-Situ Spectrophotometers Installation and Maintenance

Submersible spectrophotometers are well suited for use in streams, however, chemical and biological fouling has been a concern in past studies. Therefore, the probes were not initially deployed directly (Figure 13) in the canal. Instead, peristaltic pumps (3) drew water from the stream to the spectrophotometer (7). The spectrophotometers then measured the absorbance of the water in the UV-Visible range before the pump returned the water to the stream (1). A microcontroller (4) programmed in-house conducted this ensemble. The pumping and measurement time intervals were minimized in order to reduce the duration that waterborne contaminants would be in contact with the spectrophotometer lenses to reduce fouling (J Randall Etheridge, Birgand, Burchell, & Smith, 2013). The microcontroller in combination with a 10-gallon freshwater holding tank (9) and windshield washer pump (10) automatically rinsed the lenses with fresh water after each measurement, further minimizing exposure (J Randall Etheridge et al., 2013). During biweekly maintenance visits the absorbances of DI water and air

were measure through “dirty” lenses. Lenses were then cleaned with 5% hydrochloric acid (HCl) and a cleaning brush. Absorbances of DI water and air were measured repeatedly between multiple iterations of cleaning until the values reached acceptable levels (less than 10 m^{-1} across the spectrum) or remained constant. Lenses were considered clean if the absorbance for the fingerprint begins between 0 and 14 and declines to a value below four in the 750 nm wavelength range (Etheridge et al., 2014; Flemming, 2011; Whelan and Regan, 2006). The differences in absorbance before and after cleaning are an indicator of the degree of chemical and biological fouling that took place between site visits.

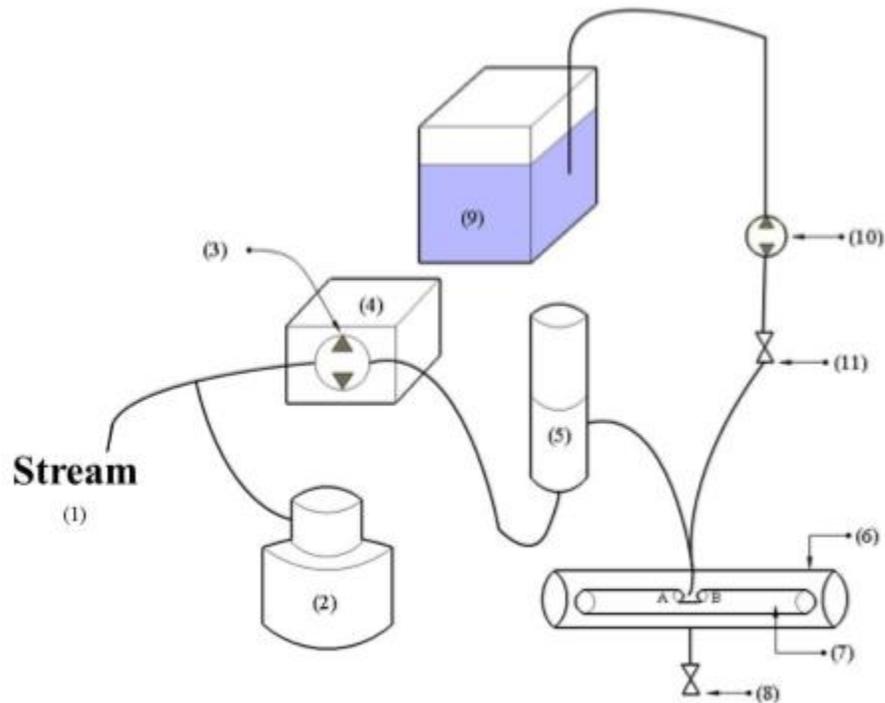


Figure 13. Schematic of monitoring system used in Lin et al., (2017).

In the final iteration of the monitoring stations used for post-restoration, the spectrophotometers were equipped with original equipment manufacturer (OEM) mechanical wipers in lieu of the freshwater cleaning system. The wipers interfaced directly with the spectrophotometer control systems. Additionally, due to the reduced fouling found during the

first year of monitoring, we installed the spectrophotometers directly in the stream. The spectrophotometer-wiper combination eliminated the need for the microcontroller system, decreasing the frequency of measurement error.

Monitoring System Designs

Monitoring System used by Lin (2017) (v1.0)

The monitoring system implemented by Lin (2017) and described above was the blueprint for the system used during the post-restoration period of this study.

Initial Post-Restoration System: Low Elevation Boxes, Spectrophotometer in Box (v2.0)

Two raised platforms, one-meter high, were constructed adjacent to the downstream end of each flume. Two separate boxes were mounted atop each of the platforms. The boxes protected water sensitive equipment from rainfall while the elevation of the platforms protected equipment from flooding during rain events. One box contained the automatic discrete sampler (2) while the second box housed all of the remaining monitoring equipment described below in System v1.0 Operation.

There was no connection to an electrical grid at any of the proposed monitoring stations, so each station was required to produce and store its own power. Each monitoring station was equipped with a 12V - 8 Ah battery for box #1 and a 120-Watt solar panel (mounted on stilts), solar charge controller, and 12V Flooded Marine Battery to power box #2. Boxes were wired separately to prevent total electrical failure if one component failed. We replaced depleted batteries with a charged battery, if a station failed to maintain enough charge on a battery over the course of the 2-week monitoring period. Depleted batteries were charged with a conventional 110Vdc battery charger. The first iteration, post-restoration, however, did not pump water to the

multi-parameter sonde from the stream; instead, the sonde was mounted to a surfboard and immersed in the stream (Fig. 5).

Low Elevation Boxes, Spectrophotometer in Stream (v2.1)

Due to mechanical failures, attributed to the repurposed peristaltic pumps, we mounted the spectrophotometers to surfboards in the stream. The freshwater cleaning system remained in place. With no need to pump water from the stream to spectrophotometer, we removed the peristaltic pump from the monitoring boxes. The microcontroller remained in place to control the freshwater cleaning system.

High Elevation Boxes, Spectrophotometer in Stream (v2.2)

On April 24-25, 2017, 87.1 mm (3.43 in.) of rain caused severe flooding at the restoration site, similar to Hurricane Matthew. What we failed to account for is the location of The Canal with respect to the floodplain of the Little River. When the Little River crests its banks, the floodwaters naturally flow towards the lowest point; in this case, the priority 2 restoration located roughly 1.8 m below the Little River's floodplain. The erosive floodwater after Hurricane Matthew and during the event in late April 2017 damaged several sections of the restoration, which NCDOT repaired in late August/early September 2017.

During the April 2017 flooding, the ADVm recorded the stage of the stream as high as 2.8 meters above the invert of the flume, before the flooding caused electrical failure at all stations. Afterwards, the station boxes were elevated to approximately three meters above the restored floodplain to prevent future damage (i.e. above the Little River floodplain). Due to the increased elevation, the freshwater cleaning system was no longer practical. Instead, a pressurized air cleaning system controlled by the spectrophotometer was installed temporarily until OEM mechanical wipers arrived. The microcontroller, windshield washer pump, valve and

freshwater tank, were removed from each station. The wiper units were installed shortly after arrival and the pressurized air cleaning system was removed. The mechanical wipers integrated seamlessly with the control terminal for the spectrophotometers and were programmed to begin cleaning 30 seconds prior to each measurement. The lenses were cleaned for 25 seconds followed by a 5-second delay, at which point the spectrophotometer initiated a measurement. All stations were operational again on 9 June 2017.



Figure 14. Left, looking upstream from HWY-70 shows standing water retained on the floodplain for up to a week following heavy rains on April 24th & 25th. Photo taken April 28th; Right, looking downstream at HWY-70 shows the same section in its normal state on May 11th after flooding subsided.

The power supply was also changed for the automated samplers after the platforms were raised, because the 12V – 8Ah batteries failed more frequently due to the increased pumping height. The automated samplers were wired to a dedicated 12V marine battery equipped with a solar panel and charge controller. The solar panel recharged the battery between 14-hour pumping intervals and the increased capacity ensured that the sampler did not fully drain the battery during cloudy weather.

Data Collection and Site Maintenance

A two-person team conducted data collection and site maintenance every two weeks. Data is downloaded from all instruments, and the discrete water quality samples are transferred

to coolers and transported to a laboratory for analysis. All equipment was physically or chemically cleaned and calibrated. During the growing season, any vegetation blocking walkways was removed. Table 4 lists the instruments used during monitoring, which parameters were collected with each instrument and how frequently these were collected.

Table 4. Sampling Scheme Summary.

Generic Name	UV-Vis Spectrophotometer	Discrete Sampler	Grab Samples	Doppler Velocity Meter
Purpose	Spectral Data	Local Calibration of Spectral Data	Degradation study of Discrete Samples	Velocity & Stage
Frequency	15 minutes	14 hours	2 weeks	15 minutes
Analyzed for	NH ₃ , TKN, TSS, DOC, TP, PO ₄ ,	NH ₃ , TKN, TSS, DOC, NO _x , TP, PO ₄	NH ₃ , TKN, TSS, DOC, NO _x , TP, PO ₄	Flowrate

Lab Analysis

Temporally stratified samples that were distributed regularly across the 2-week period were selected for laboratory analysis. Sudden increases in either velocity measured by the ADVN or spectrophotometer absorbance qualified samples for preferential analysis in addition to the standard temporal spread. This preferential sample selection approach creates greater concentration stratification of samples (Lin, 2017). We refrained from acidifying samples to analyze samples for ammonium, orthophosphates, and DOC. The samples were separated into two aliquots at the lab. The first aliquot required 140 ml of each discrete sample to be filtered to obtain a 40 ml solution. The filtered solution was used for measuring concentrations of ammonium, nitrate, orthophosphate and DOC in each sample. The remainder of the discrete

sample was analyzed for TKN, TP and TSS. Table 5 lists the EPA method used to analyze each analyte.

Table 5. Analyte and EPA methods used by the EAL (Dr. Cong Tu, Personal Communication).

Analyte	Method	Detection Limit (mg/l)
TKN	Standard Methods 4500-Norg B, Bran & Leubbe Autoanalyzer III	0.03
NH ₃	EPA Method 351.2	0.01
NO ₃ ⁻	EPA Method 353.2	0.01
TP	EPA Method 365.4	0.03
PO ₄ -P	EPA Method 365.1	0.01
TSS	EPA Method 160.3	0.5
DOC	EPA Method 415.1 with Teledyne Tekmar Apollo 9000, 0.45 µm filter	0.01

Degradation Study

The 52-mile distance to the site limited ease of access and directly affected the monitoring setup. Discrete samples could not be transported back to NCSU daily. This in combination with refraining from acidifying the discrete water quality samples required us to conduct a sample degradation study to determine if samples changed while in the sample bottles. Three pairs of grab samples were collected taken at each of the monitoring stations during bi-weekly maintenance visits. The first of each pair was returned to the lab and refrigerated while the second grab sample was left inside the discrete sampler and collected during the following maintenance visit. A paired T-Test was used to determine if there was a concentration difference between samples brought back to the lab immediately and those left in the samplers for two weeks. Samples were deemed significantly different if the paired T-Test returned a p-value less than 0.05.

Method to calculate concentrations from absorbance data

We predicted high-frequency concentration data using absorbance data collected by in-situ UV-Vis spectrophotometers coupled with preferentially selected discrete samples.

Spectrophotometers function by firing a beam of light across a measurement window and measuring the frequency of the incoming wavelengths. The device compares the wavelengths of the incoming light to a reference measurement collected from a secondary beam that does not pass through the measurement window. The difference between these two measurements is the absorbance. The spectrophotometers used in this study are equipped with a ‘global calibration’, a method used to correlate the absorbance data with parameters known to absorb light (e.g. DOC, nitrate and TSS). While the ‘global calibration’ functions well to calculate parameter concentrations, more precise calibrations can be achieved using Partial Least Square Regression (PLSR). Applying PLSR to the absorbance data has also been proven to predict concentrations of parameters that do not absorb light (J R Etheridge et al., 2014). The regressions we created using predicted concentration data from discrete water quality samples stratified temporally and across a range of concentrations in order to provide the best possible calibration (Lin, 2017).

Calculating Nutrient Loading, Cumulative Loads and Cumulative Volumes

Cumulative load (L) passing through each station was calculated by multiplying the measured pollutant concentration (C) at a given time (t) with the flow rate (Q) through the flume at the same instance. In this study, the time (t) is the 15-minute measurement interval of the instruments.

$$L = C_t * Q_t dt \quad \text{(Equation 2)}$$

Data Quality Assurance

Flow Data

Missing or erroneous flow data was corrected with different methods depending on the quantity of data in question. First, velocity data was plotted to visually identify outliers from the surrounding velocity pattern. Identified potential erroneous data points were removed manually,

resulting in data gaps. Event or threshold detection were not employed. Second, data gaps and small amounts of noise were smoothed by applying a double moving average. The moving average was applied using 3 or 10 data points above and below the data point in question, resulting in a 7 or 21-point band for calculating the average. The flow conditions determined which width to use for the moving average. The widest band was applied during base flow because changes in velocity were less prone to sudden changes. Leading up to storm events and during the falling limb of a storm events the narrower band was used so that the velocities were not over or underestimated. During storm events the raw velocity measurements, were accepted without applying a moving average. The moving average failed if the gaps were greater than or equal to the band width used, so a linear interpolation was used to fill any remaining gaps. The process of removing erroneous data points was subjective at times. In retrospect, automatic detection or detection and removal should be applied. Automatic detection increases the objectivity (i.e. reproducibility) of the method.

Spectral data

Due to equipment failure or misuse, data collected by the spectrophotometers contained M|E data points. As mentioned previously, improvements to the system design reduced the quantity and frequency of these occurrences. Spectral data was removed based on two factors using “R” (R Core Team, 2017). First absorbance data was checked for completion (measurements containing no ‘NA’ readings in any of the 2.5 nm spectral increments in the 220-732.5 nm range). Absorbance data with one or more ‘NA’ readings were excluded. Second, any obvious outliers that did not correspond with changes in flow or were physically inconceivable were filtered out using “R” and the Aquarius software (R Core Team, 2017; Aquatic Information Inc., 2009).

Peaks and troughs in data were validated by comparing each station's chemographs for DOC and nitrate, individually, to the hydrograph for that station. DOC rises in conjunction with a rise in flow, so any individual peaks in DOC that occurred during base flow was considered noise and omitted (Lin, 2017). Nitrate concentrations peaked briefly at the beginning of a storm event but was heavily diluted for the remainder of the event. Therefore, erratic dips in nitrate concentrations that did not correspond to flow events were removed. When handling the larger time series data sets, "R" was used to filter out erroneous concentration data based on date and time, parameter concentration, or a combination of the two (e.g. remove any point between 1 April and 5 May above 99 mg/L DOC).

Larger data gaps that resulted from equipment failure or removal of sections of erroneous data were 'patched' with 15-minute data linearly interpolated from discrete sample data, where available. Because discrete samples were preferentially selected for analysis around rain events, we were able to recreate the chemographs of events in the absence of absorbance data.

The PLSR code used to predict values between DOC and nitrate concentrations from spectral data would, depending on the data and calibration used, predict values that are below the detection limit of the laboratory testing equipment used to analyze the discrete samples. When concentrations were predicted below the detection limit, the program automatically rounded up to one-half of the detection limit, i.e. 0.05 mg/l and 0.005 mg/l for DOC and NO₃, respectively. PLSR frequently predicted nitrate concentration below the detection limit for the spring/summer period. These instances were of note because the PLSR prediction was the inverse of the values predicted by the global calibration. We hypothesized that the number of data points and range of concentrations of these data played a role in this behavior.

1.5 Results and Discussion

Monitoring conducted pre-restoration by Lin yielded consecutive data from November 2013 until March 2015, for all three monitoring stations (Lin, 2017). Monitoring conducted post-restoration, from January 2017 until January 2018, yielded consecutive data for all three monitoring stations for a 6-month period from June 2017 until January 2018.

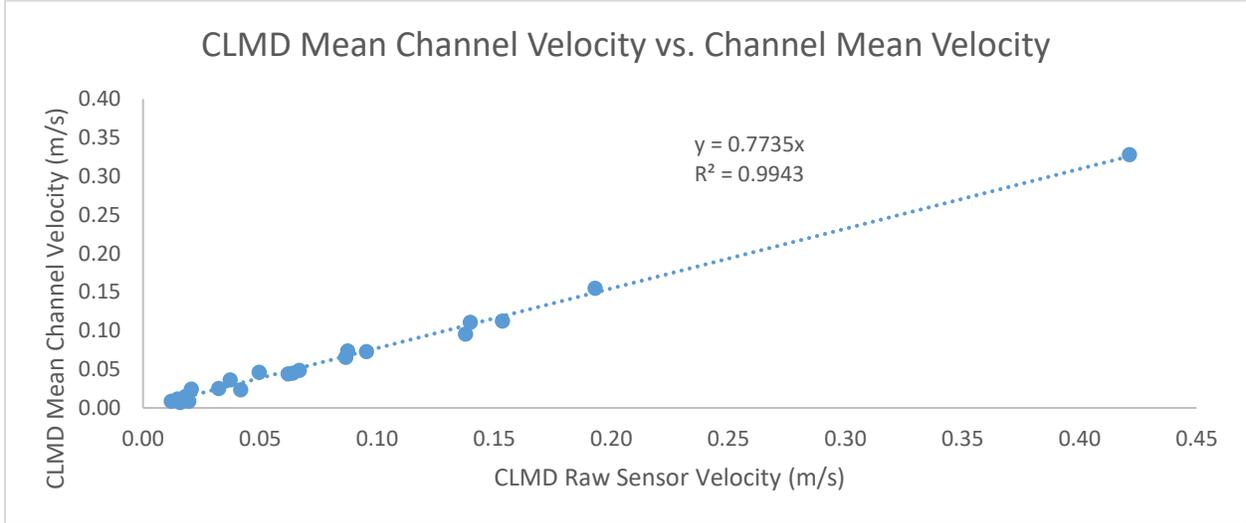
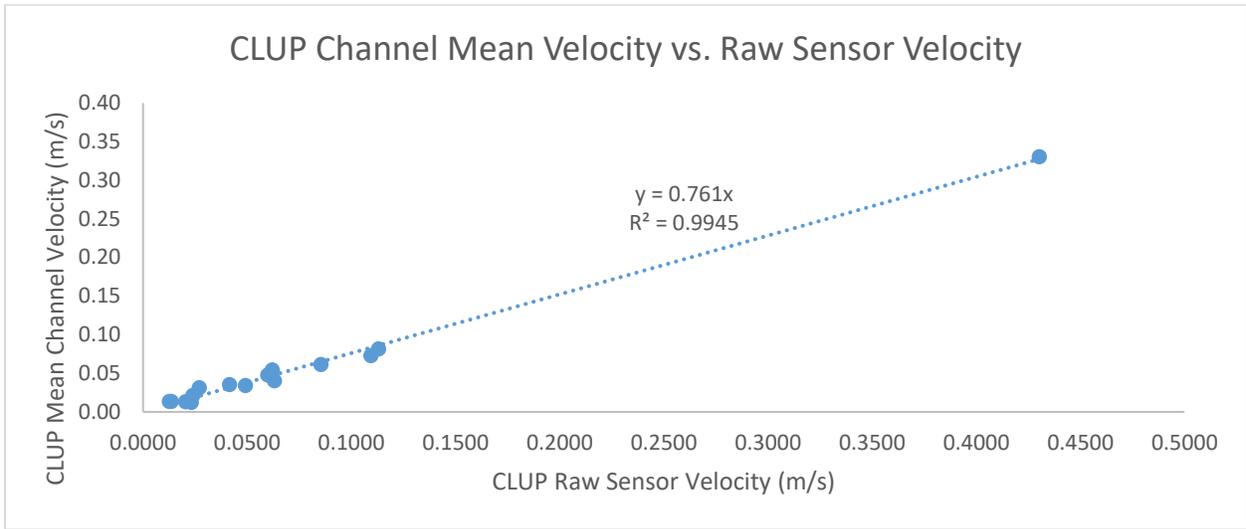
Creating Index Velocity Ratings to Calculate Flow

The mean cross-section velocities were equal to 76.10% ($R^2=0.9945$), 77.35% ($R^2=0.9941$) and 83.03% ($R^2=0.9929$) of the ADVN velocities at CLUP, CLMD, and CLDN, respectively. The ADVN was overestimating velocities that passed through each station by 23.90%, 22.65%, and 16.97%, respectively. The monitoring stations built for the post-restoration period overestimate the channel velocities more than those in the pre-restoration period did. The index velocity ratings are compared in Table 6. We hypothesized that the decrease in index velocity ratings compared to those established in by Lin et al. (2017) may have been due to wider flume inverts used during this study, but also due to a firmware update of the sensors (Lin, 2017). The increased influence of the wind on the restored stream channel due to decreased stream bank height and a lack of surrounding vegetation may have contributed to more turbulent flow and noisier velocity data, but this does not affect the velocity rating (Lin, 2017). By multiplying the raw sensor velocities by the slope of the regression, we were able to calibrate the sensor to the mean channel velocity. We were then able to use the calibrated sensor velocities to calculate the flow each station.

Table 6. Comparison of the correction factors derived from the index velocity ratings from Pre- and Post-Restoration.

	Pre-Restoration		Post-Restoration	
	Correction Coefficient	R^2	Correction Coefficient	R^2
CLUP	97.57%	0.9858	76.10%	0.9945

CLMD	93.02%	0.9889	77.35%	0.9943
CLDN	98.91%	0.9838	83.03%	0.9929



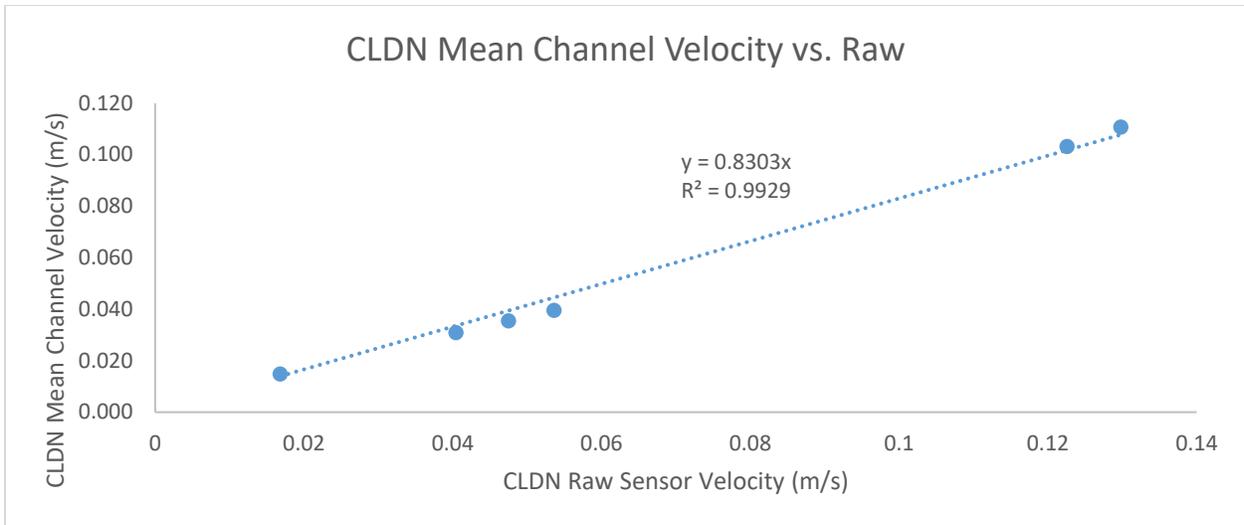


Figure 15. Raw Sensor Velocity versus Mean Channel Velocity (a) CLUP; (b) CLMD; (c) CLDN (top to bottom).

Degradation Study Results

There were no statistically significant differences between the samples returned to the lab immediately and left in the sampler for two weeks (Table 7). As a result, we concluded that the concentration data obtained from discrete samples could be used for our analyses.

Table 7. Results of the paired T-test used to test for degradation between GS-A and GS-B for Spring/Summer (top) and Fall/Winter (bottom). Alpha = 0.05.

Station		TKN	NH ₄ -N	NO ₃ -N	TP	PO ₄ -P	TSS	DOC
Spring and Summer								
CLUP	Mean A	1.20 ±0.60	0.047 ±0.042	1.51 ±1.77	0.27 ±0.23	0.012 ±0.0052	19.1 ± 36.0	4.06 ±1.74
	Mean B	0.93 ±0.18	0.042 ±0.046	2.08 ±1.97	0.29 ±0.30	0.013 ±0.013	19.28 ± 35.8	4.14 ±1.32
	p-value	0.3929	0.7452	0.1547	0.8922	0.9551	0.8559	0.9279
	Mean of differences	0.2715	0.0040	-0.568	-0.0120	-0.0003	-0.1825	-0.0775
CLMD	Mean A	0.972 ±0.66	0.044 ±0.048	1.28 ±1.78	0.068 ±0.048	0.006 ±0.0089	7.362 ±12.267	4.692 ±1.541
	Mean B	0.888 ±0.17	0.026 ±0.021	0.59 ±0.45	0.082 ±0.067	0.006 ±0.0055	9.22 ±14.95	4.436 ±0.536
	p-value	0.8291	0.3301	0.4507	0.2262	1.00	0.8534	0.7615
	Mean of differences	0.0840	0.0180	0.6880	-0.0140	0.00	-1.8580	0.256
CLDN	Mean A	1.353 ± 0.588	0.0433 ±0.067	0.7 ±0.685	0.1067 ±0.045	0.02 ±0.035	10.71 ± 12.39	5.42 ±0.97
	Mean B	0.756 ±0.271	0.01 ±0.01	0.883 ±0.764	0.1833 ±0.0666	0.0067 ±0.012	22.31 ±30.74	4.833 ±0.125
	p-value	0.3551	0.4226	0.1354	0.08583	0.6349	0.3908	0.4199
	Mean of differences	0.4067	0.0330	-0.1833	-0.0767	0.0133	-0.1161	0.5867

Table 7. (continued).

Station		TKN	NH ₄ -N	NO ₃ -N	TP	PO ₄ -P	TSS	DOC
Fall and Winter								
CLUP	Mean A	1.17 ±1.25	0.06 ±0.04	3.31 ±0.69	0.30 ±0.73	0.022 ±0.019	2.19 ±1.89	3.59 ±1.70
	Mean B	0.87 ±0.53	0.082 ±0.06	3.31 ±0.52	0.12 ±0.20	0.025 ±0.022	2.54 ±2.04	3.81 ±1.75
	p-val	0.4606	0.3083	0.9813	0.4378	0.7418	0.5992	0.6755
	Mean of differences	0.30	-0.0191	-0.0042	0.1817	-0.0025	-0.3525	-0.2192
CLMD	Mean A	1.59 ±1.39	0.083 ±0.087	2.13 ±0.96	0.081 ±0.066	0.019 ±0.0302	0.9967 ±1.066	3.998 ±0.766
	Mean B	0.76 ±0.44	0.068 ±0.060	2.35 ±1.07	0.195 ±0.448	0.0175 ±0.021	0.9775 ±1.292	3.587 ±1.253
	p-val	0.1053	0.4873	0.5917	0.3722	0.7774	0.9698	0.2773
	Mean of differences	0.8320	0.0150	-0.2217	-0.1140	0.0017	0.0192	0.4110
CLDN	Mean A	1.081 ±0.222	0.0475 ±0.0349	1.699 ±0.704	0.0536 ±0.04	0.02 ±0.024	0.6863 ±0.899	3.975 ±0.938
	Mean B	1.244 ±0.418	0.0825 ±0.0305	1.740 ±0.645	0.0575 ±0.0378	0.0225 ±0.034	0.7087 ±1.39	4.054 ±0.825
	p-val	0.4286	0.0509	0.687	0.8419	0.7406	0.966	0.8251
	Mean of differences	-0.1625	-0.0350	-0.0413	-0.00375	-0.0025	-0.0225	-0.0788

Discrete Sample Summary

Table 8. Summary of the discrete samples collected during the monitoring period.

	TKN	NH ₄ -N	NO ₃ -N	TP	PO ₄ -P	TSS	DOC
CLUP							
No. Samples	184	184	184	184	184	184	184
Mean ± SD	1.04 ±0.76	0.08 ±0.08	3.08 ±0.85	0.25 ±0.76	0.02 ±0.04	4.61 ±10.85	3.99 ±1.63
Minimum	-0.09	0.00	0.15	0.00	0.00	0.00	1.84
Maximum	5.12	0.78	4.99	7.53	0.38	93.44	9.98
CLMD							
No. Samples	191	191	191	191	191	191	191
Mean ± SD	1.10 ±0.74	0.10 ±0.48	1.54 ±1.01	0.13 ±0.2	0.02 ±0.03	4.42 ±9.59	4.88 ±1.54
Minimum	0.05	0.00	0.00	0.00	0.00	0.00	0.66
Maximum	6.71	6.61	4.36	1.61	0.24	74.07	9.27
CLDN							
No. Samples	139	140	140	139	140	139	140
Mean ± SD	1.10 ±0.4	0.08 ±0.11	1.37 ±0.76	0.11 ±0.12	0.02 ±0.03	5.60 ±13.34	5.15 ±1.65
Minimum	0.37	0.00	0.00	0.00	0.00	0.00	1.84
Maximum	2.42	1.18	4.09	0.49	0.14	101.43	19.05

PLSR Analysis and Summary

After conducting the degradation study on the grab samples collected in the field, discrete samples were divided by spring (20 March) and fall (22 September) Equinoxes for 2017. Seasonal separation was used to create two different PLSR models for Nitrate and DOC at each three stations. The first model used all discrete samples collected during the fall/winter period while the second used discrete samples collected during the spring/summer period. The best model for each period was based on the combination of the best R^2 and the lowest number of components that yielded the lowest RMSEP (Table 9).

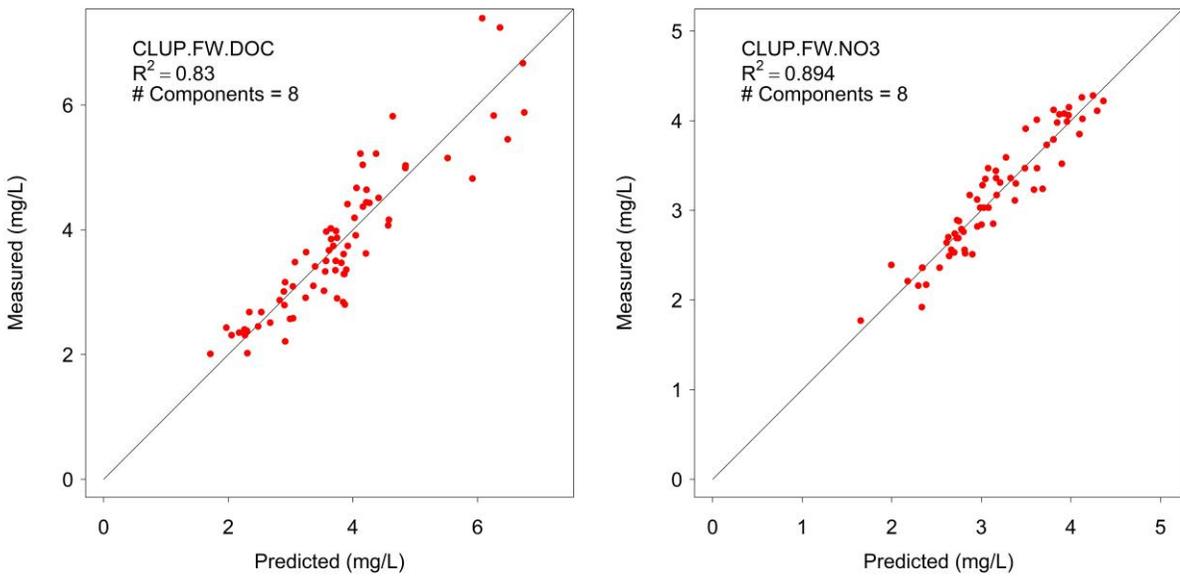


Figure 16. Regression relationships between measure DOC (left column) and nitrate (right column) from discrete sampling and PLSR predictions; CLUP, CLMD and CLDN from top to bottom.

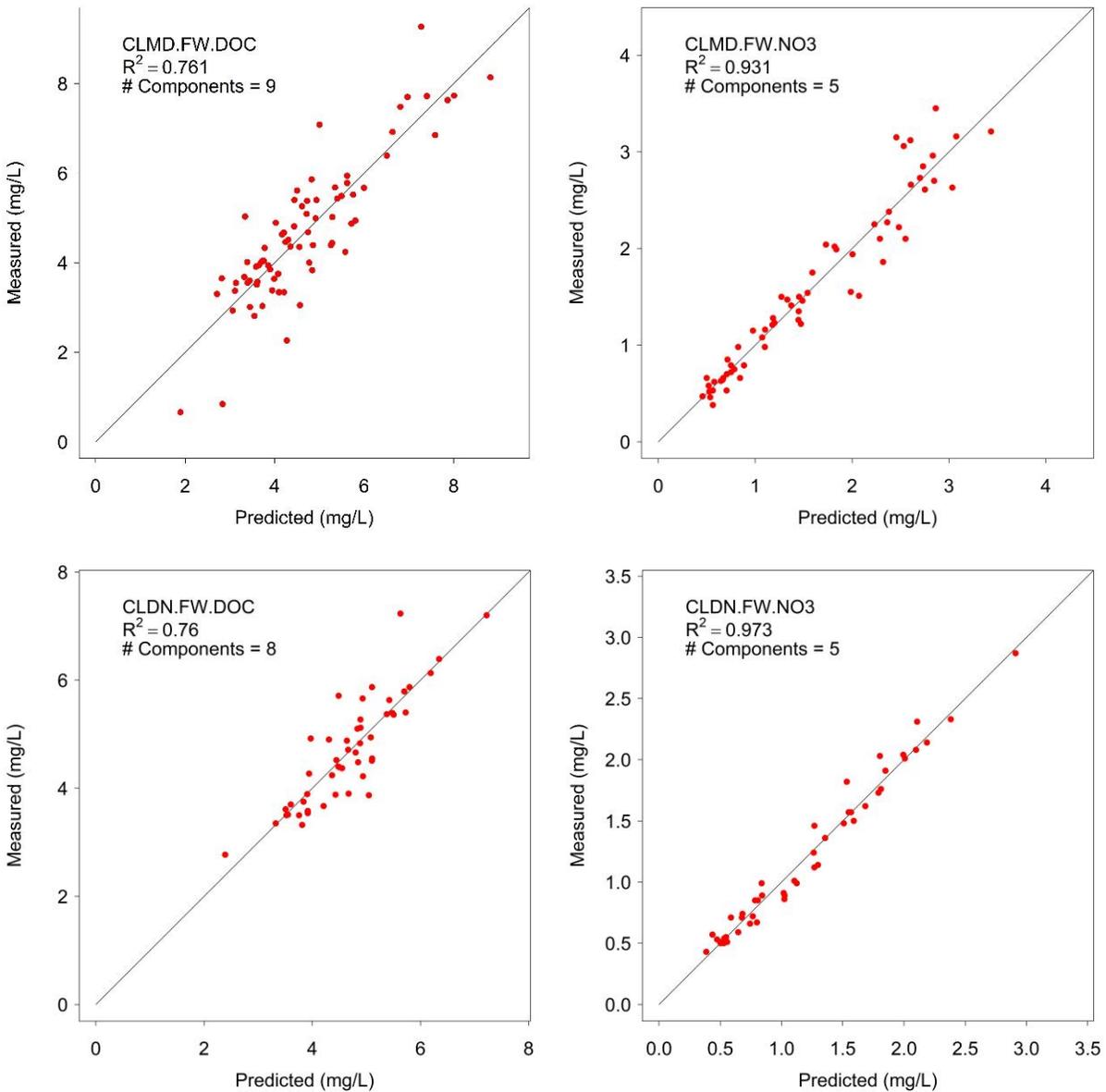


Figure 16. (continued).

We found the best regression relationships between our discrete samples and the predicted values from PLSR for DOC and nitrate (see Figure 16), as indicated by the dimensionless goodness-of-fit indicator, the Nash Sutcliffe Efficiency (NSE), values above 0.8 (Table 9) (Ritter & Muñoz-Carpena, 2013). A model (in hydrology, *sensu* Ritter & Muñoz-Carpena, 2013) is considered satisfactory when NSE are above 0.65. According to this criterion, regressions were acceptable for other parameters some of the time. However, it appears that

regressions were not acceptable particularly for phosphate and ammonium. About half of the regressions appeared acceptable for TKN and TP. Typically, and confirming what Lin (2017) found, regressions were poor when the calibration concentration range was poor. Because regressions for nitrate and DOC were consistently good to very good (*sensu* Ritter & Muñoz-Carpena, 2013), these two parameters were the only ones used to calculate the restoration impacts.

Table 9. Summary of all PLSR calibrations for all seasons, stations and parameters. * denotes NSE values that are unsatisfactory.

	TKN	NH ₄ -N	NO ₃ -N	TP	PO ₄ -P	DOC
CLUP in spring and summer						
No. Observations	55	41	47	44	58	50
No. PLSR Components	5	6	6	6	5	5
R ²	0.718	0.576	0.913	0.897	0.516	0.904
RMSE	0.34	0.05	0.34	0.12	0.06	0.57
NSE	0.72	0.58*	0.91	0.9	0.52*	0.9
CLMD in spring and summer						
No. Observations	15	9	15	15	18	17
No. PLSR Components	4	5	4	6	5	6
R ²	0.769	0.968	0.94	0.885	0.719	0.877
RMSE	0.37	0.12	0.4	0.91	0.03	1.33
NSE	0.74	0.89	0.94	0.85	0.5*	0.88
CLDN in spring and summer						
No. Observations	20	8	15	12	18	18
No. PLSR Components	6	5	6	5	5	5
R ²	0.249	0.123	0.9	0.897	0.0005	0.883
RMSE	0.26	0.04	0.21	0.04	0.02	0.56
NSE	0.18*	-3.04*	0.78	-0.03*	-0.02*	0.82

Table 9. (continued).

	TKN	NH₄-N	NO₃-N	TP	PO₄-P	DOC
CLUP in fall and winter						
No. Observations	70	62	65	47	73	63
No. PLSR Components	5	5	8	6	5	8
R ²	0.376	0.743	0.894	0.905	0.394	0.83
RMSE	0.33	0.04	0.39	0.09	0.02	0.51
NSE	0.38*	0.74	0.89	0.9	0.39*	0.81
CLMD in fall and winter						
No. Observations	68	76	63	56	76	64
No. PLSR Components	5	5	5	5	5	9
R ²	0.277	0.245	0.931	0.515	0.213	0.76
RMSE	0.28	0.07	0.31	0.06	0.02	0.62
NSE	0.28*	0.25*	0.93	0.52*	0.21*	0.83
CLDN in fall and winter						
No. Observations	41	37	47	42	50	42
No. PLSR Components	6	5	5	5	5	8
R ²	0.828	0.384	0.973	0.951	0.293	0.76
RMSE	0.26	0.02	0.21	0.04	0.02	0.43
NSE	0.83	0.38*	0.97	0.95	0.29*	0.86

Table 10. Summary of PLSR calibration for TSS for all three stations (CLUP, CLMD, CLDN) using the entire monitoring period. * denotes NSE values that are unsatisfactory.

	CLUP	CLMD	CLDN
No. Observations	98	96	68
No. PLSR Components	7	5	7
R ²	0.66	0.28	0.307
RMSE	4.11	6.12	3.27
NSE	0.66	0.28*	0.31*

Continuity of Flow across Monitoring Periods

In order to determine if there is an effect on water quality due to the restoration of The Canal, we first had to determine if there was a change in flow relationship between our monitoring stations and the reference before and after restoration. Changes in land use or land cover within the watershed and climatological variations have an impact on the flow relationships of the reach. Pre-restoration monitoring in 2014 and post-restoration monitoring in 2017 had a total of 1,524 mm and 1,260 mm of rainfall respectively according to the weather station at Cherry Research Farm located 4 km from The Canal (NC Climate Office). The 2014

monitoring period contains a brief drought period for no more than 10% of the county. The 2017 monitoring period on the other hand contains two extended drought periods affecting 95-100% of the county (Figure 17).

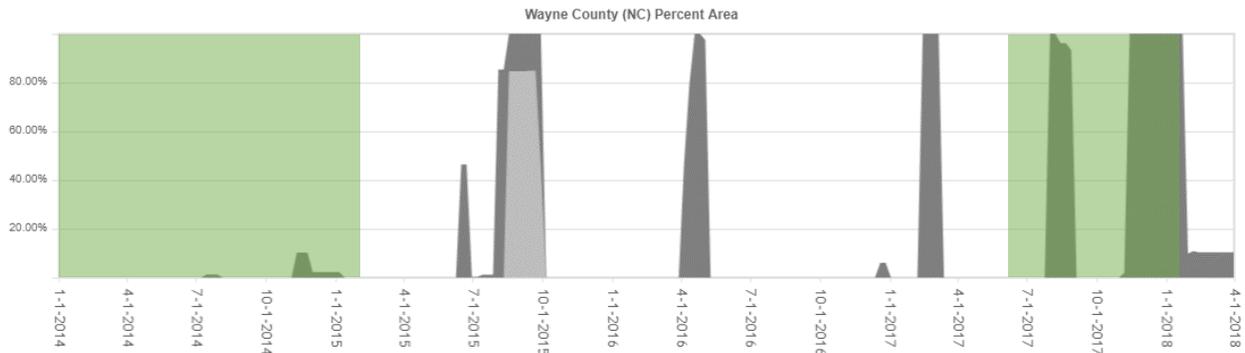


Figure 17. Timeline of drought conditions in Wayne County, NC from 2014-2018. 6-month monitoring periods in green. (Dark gray = abnormally dry, light gray= moderate drought).

Cumulative flow through the treatment stations, CLMD and CLUP, were plotted against the reference station, CLUP. The cumulative flows from both monitoring periods were plotted end to end by using the final cumulative flow value from pre-restoration as the initial value for the post-restoration cumulative values. Results are shown in figures 19 and 20. The flow relationships for the post-restoration period for both CLMD (solid) and CLDN (dashed) are consistent with the relationships of the last three months of the pre-restoration period.

The slopes of the relationships for pre- and post-restoration are worthy of discussion. Initially data for the entire monitoring period was used to evaluate the continuity of the relationship. However, two large increases at approximately 500 mm and 580mm on the x-axis (Reference) skewed the relationship. The two deviations are the result of water entering the reach from the Little River via UT2. Not shown on most maps of the area, UT2 drains into The Canal to the west and the Little River to the east. Therefore, when stage in the Little River was high enough it would flow into The Canal. These events are different from the event witnessed during the week of 24 April 2017 when the Little River crested its banks and caused water to flow into The Canal. In the two pre-restoration events, water only rose high enough to connect via UT2.

The additional flow from the Little River sharply increased flow through the treatment stations. Without any change in flow through the reference station, the relationships were skewed. Therefore, the relationships for all parameters were initially plotted with these periods (25/12/2014 until 30/12/2014 and 14/01/2015 until 18/01/2015) removed (Figure 18). Plot for all parameters with the Little River events included are found in Appendix E. When compared without the two Little River events, the relationship indicated a 16.0% and 13.4% decrease in flow from pre-restoration for CLMD and CLDN.

Because the Little River events were removed subjectively, only the last three months of pre-restoration data were used to evaluate quantitatively the differences between the two monitoring periods (Figure 18). Using the adjusted cumulative volume data, confirmed the results from visually evaluating the continuity. The large rainfall events also affected the DOC and nitrate data, so the same approach for continuity analysis of these parameters was applied. The relationships between cumulative flow volumes show no apparent inflection points but do show small differences.

Using only the last three months of pre-restoration data produced percent differences of -3.8% and -1.1% for CLMD and CLDN, respectively. This indicated that the flow relationships between stations has remained unchanged pre- and post-restoration. Deviations are the result of a variety of factors. First, the post-restoration flumes were different from those used during pre-restoration. The width of the trapezoidal base was narrower for the pre-restoration flumes and the side-slopes were steeper to accommodate the dimensions of the original canal. Velocity calibration and correcting for erroneous flow data also introduced some degree of error. The average cross-section velocity resulting from the calibration may differ from the velocity present in the stream and the corrections of erroneous velocity were made using best professional

judgement. Nonetheless, the flow relationships are remarkably similar for pre- and post-restoration. Deviations of more than 3.8% (CLMD) or 1.1% (CLDN) of the cumulative load relationships are strong indicators that processes other than flow errors are at play.

Table 11. Cumulative flow slopes pre-/post-restoration (* post 18-01-2015 data only).

Station vs. CLUP	Pre-Restoration		Post-Restoration	Percent change	
	All	Jan 2015 until Apr 2015		All	Jan 2015 until Apr 2015
CLMD	1.1034	0.9633*	0.9266	-16.0%	-3.8%*
CLDN	1.6003	1.4019*	1.3866	-13.4%	-1.1%*

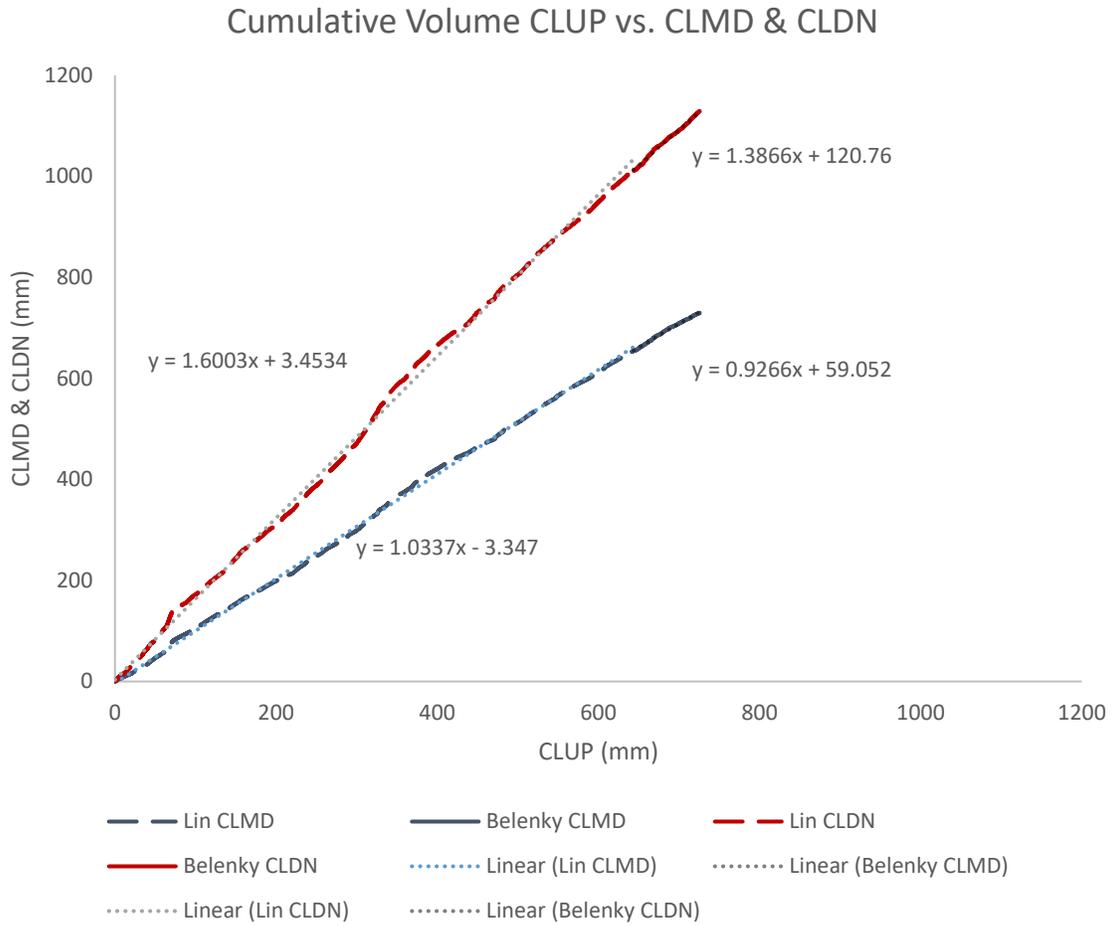


Figure 18. Cumulative Volume CLMD (blue) & CLDN (red) (mm) vs. Cumulative Volume CLUP without Little River events (dashed) and all post-restoration data (solid).

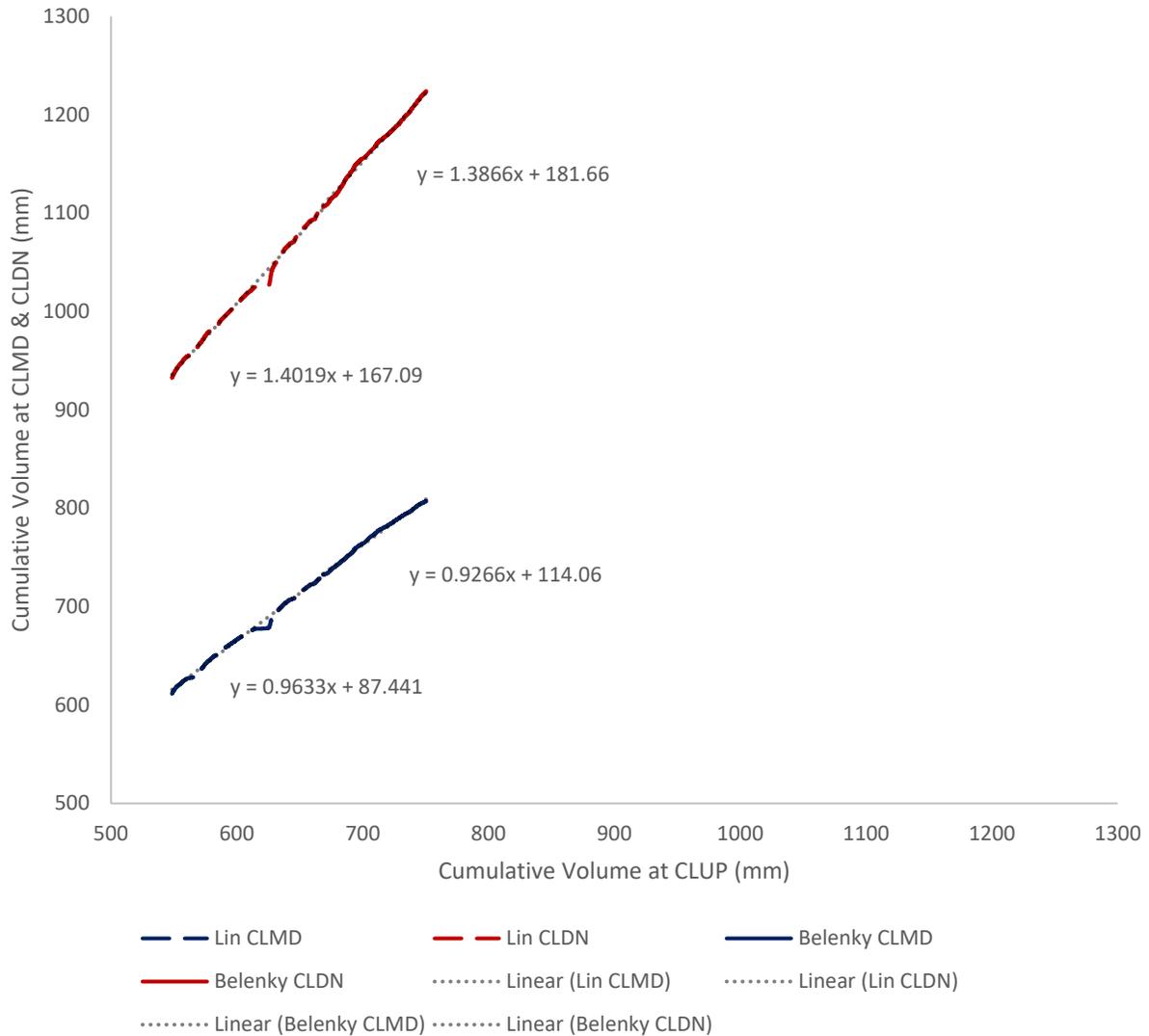


Figure 19. Cumulative Volume CLMD (blue) & CLDN (red) (mm) vs. Cumulative Volume CLUP (mm using data from Lin (2017) from 18-01-2015 onward (dashed), all post-restoration data (solid).

Change in Flow-weighted Concentration Entering at CLUP

After verifying that there were no break points in the flow relationships between pre- and post-restoration periods, it was necessary to verify no major changes in the loads entering at CLUP. To do this, the cumulative loads were plotted as a function of cumulative volume. The slope of the tangent line at any point corresponds to the instantaneous concentration, and over a given period, the slope of the line between the first and last point over the period corresponds to the flow weighted concentration over the period. The slope of the regression line through the

cumulative loads/flows, and the variations of the curves above and below the trend line can be used as indicators of hydro-chemical signatures. The slopes of the DOC trend lines from pre- to post-restoration change from 5.94 mg/L to 5.33 mg/L and those for nitrate changed from 2.81 mg/L to 2.60 mg/L, corresponding to an apparent decrease by 10% and 14% for DOC and nitrate, respectively (Figure 20). However, the apparent variations above and below the trend lines do not exhibit any obvious changes from those already observed during the pre-restoration period, suggesting that the loads and the patterns of nitrate and DOC entering the restored section at CLUP did not change significantly.

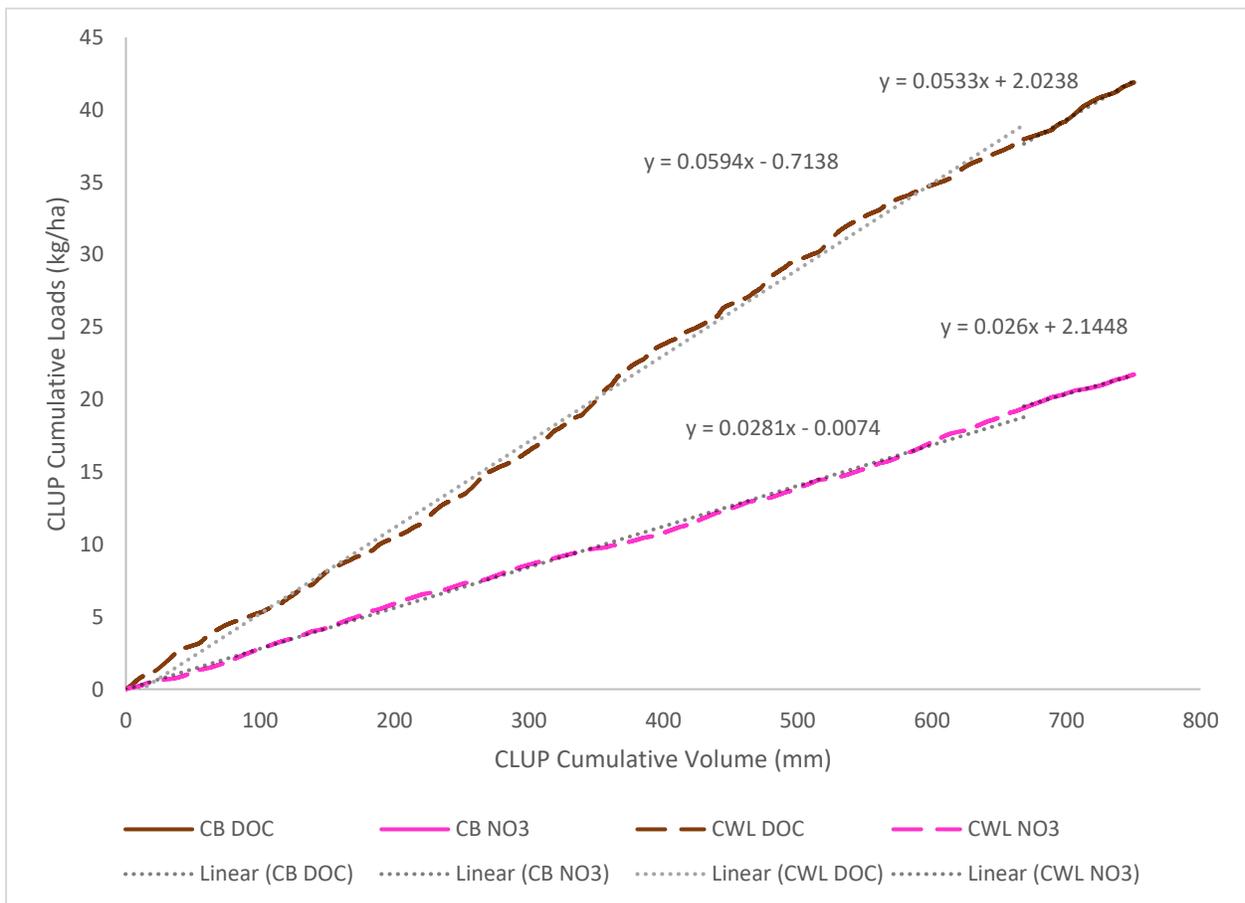


Figure 20. Flow-weighted DOC (brown) and nitrate (pink) concentrations entering CLUP using data from Lin (2017) (dashed) and data collected by Belenky (solid).

Change in Relative Cumulative DOC and Nitrate Loadings

The relative cumulative loads between CLMD and CLDN, and CLUP for DOC and nitrate exhibit relatively linear relationships, ‘interrupted’ by large intermittent load increases at CLMD and CLDN due to the intermittent connections with the Little River during large rainfall events as discussed earlier. The first year of data collected by Lin (2017) could not be used for this analysis and only the linear portion corresponding to the last three months of pre-restoration data were used.

Change in Cumulative DOC and NO₃ Loading at CLMD Relative to CLUP

During the last three months of the pre-restoration period and at CLMD, the ratios between CLMD and CLUP of the double mass curves were 1.23 and 0.83 for DOC and nitrate, respectively (Figure 23 & Figure 25). This suggests that, between the upstream and middle stations, and during the pre-restoration period, there were processes that led to relative enrichment of DOC and a relative removal of nitrate compared to the reference station. Enrichment could be due to lateral addition and in-stream processes. Removal suggests that in-stream processes offset all lateral additions from groundwater and tributaries or nitrate entering from upstream was reduced.

Following restoration, the ratios changed to 1.06 and 0.28 for DOC and nitrate, indicating a decrease in loads of both parameters between CLUP and CLMD (Figure 23 & Figure 25). The ratios decreased by 14% and 66% for DOC and nitrate, respectively. These changes are very large, and a lot larger than we expected, particularly for nitrate. The most striking results are for nitrate, because even with lateral additions between the two stations (we observed multiple instances of groundwater resurgence through the daylighting from floodplain to terrace) and from

tributary UT1 (Figure 21), which drains water from a commercial hog operation containing around 2.5 mg/L of nitrate (Qianyu Hang, personal communication).



Figure 21. Seepage entering the restoration through the daylighting.

Change in Cumulative DOC and Nitrate Loading at CLDN Relative to CLUP

Continuing our analysis with CLDN and CLUP using the same approach as before, we found that the DOC and nitrate ratios to be 1.58 and 1.25 pre-restoration and 1.61 and 0.47 post-restoration (Figure 23 & Figure 25). This is an upward inflection of 2% for DOC loading and a downward inflection of 62% (Figure 24) for nitrate loading across the whole reach. Here the interpretation is not as straight forward as for CLMD. First, for DOC the post-restoration double export curve is not as linear as the others are and exhibits several distinct phases. The overall

relative DOC export of 1.61 at CLDN is 52% higher than the 1.06 at CLMD. This suggests that between CLMD and CLDN, there were DOC additions and/or different in-stream processes than those between CLUP and CLMD. The change in nitrate relative exports at CLMD and CLDN, between pre- and post-restoration phases, are similar (66% and 62%), although the export ratios suggest that lateral addition of nitrate between CLMD and CLDN was likely during both pre- and post-restorations.

Change in Total Volumes and Loads Pre- and Post-Restoration

The very stark changes observed in the exports of nitrate between pre- and post-restoration, must be considered in context of the relative drought during the monitoring period. We have seen that the signature of the DOC and nitrate loads did not change significantly, but the total masses did, and this may be important in the overall interpretation. Starting with the upstream station, total volumes and loads per year all dropped significantly from pre-restoration to post-restoration. Volumes through CLUP decreased 71% from 1,207,761 m³/year to 355,631 m³/year. For DOC and nitrate, the decreases were 75% and 71% from 6,862 kg/year to 1,673 kg/year and 3,497 kg/year to 967 kg/year, respectively. We have also observed similar decreases in annual loading from station to station. The total mass of DOC and nitrate added (+) and removed (-) per year from CLUP to CLMD has decreased roughly by an order of magnitude for DOC from +9,340 kg/year to +1,409 kg/year and from +1,324 kg/year to -378 kg/year for nitrate (Table 12). The post-restoration values, however, were obtained during the driest months, and then scaled to 12 months, so they are not a true representation of a full year of monitoring. Rather this data represents low flow conditions. Additionally, the pre-restoration monitoring period contains three rain events that caused water to flow in from the Little River, while the two

flood events that occurred during the six-months of post-restoration monitoring were not monitored (Lin, 2017).

Table 12. Relative and measured values for all parameters pre-/post-restoration and percent changes (* post 18-01-2015 data only).

Changes relative to Upstream									
	Pre-Restoration			Post-Restoration			Percent change		
	Volume	DOC	NO3	Volume	DOC	NO3	Volume	DOC	NO3
CLMD	1.034	1.4368	0.7805	0.9266	0.9634	0.2876	-10.4	-32.9	-63.2
	0.9478*	1.2376*	0.8105*	-	-	-	-2.2*	-22.2*	-64.5*
CLDN	1.600	1.9338	1.1544	1.3866	1.4667	0.4356	-13.3	-24.1	-62.3
	1.4074*	1.5933*	1.2674*	-	-	-	-1.5*	-7.9*	-65.6*
Changes in total volume and mass									
	Volume (m3)	DOC (kg)	NO3 (kg)	Volume (m3)	DOC (kg)	NO3 (kg)	-	-	-
CLUP	1,533,857	8,715	4,441	195,597	933	552	-	-	-
CLMD	2,711,676	20,577	6,123	312,022	1,847	321	-	-	-
CLDN	5,785,961	28,894	9,089	675,738	3,005	525	-	-	-
Changes in total volume and mass per year									
	Volume (m ³ /yr.)	DOC (kg/yr.)	NO3 (kg/yr.)	Volume (m ³ /yr.)	DOC (kg/yr.)	NO3 (kg/yr.)	Volume	DOC	NO3
CLUP	1,207,761	6,862	3,497	355,631	1,673	967	-70.6	-75.3	-71.4
CLMD	2,135,178 +927,417	16,202 +9,340	4,821 +1,324	567,313 +211,382	3,082 +1,409	589 -378	-73.4	-79.3	-87.9
CLDN	4,555,875 +2,420,697	22,751 +6,549	7,157 +2,336	1,228,615 +661,302	5,296 +2,215	887 298	-73.0	-76.0	-86.7

Cumulative DOC CLUP vs. CLMD & CLDN

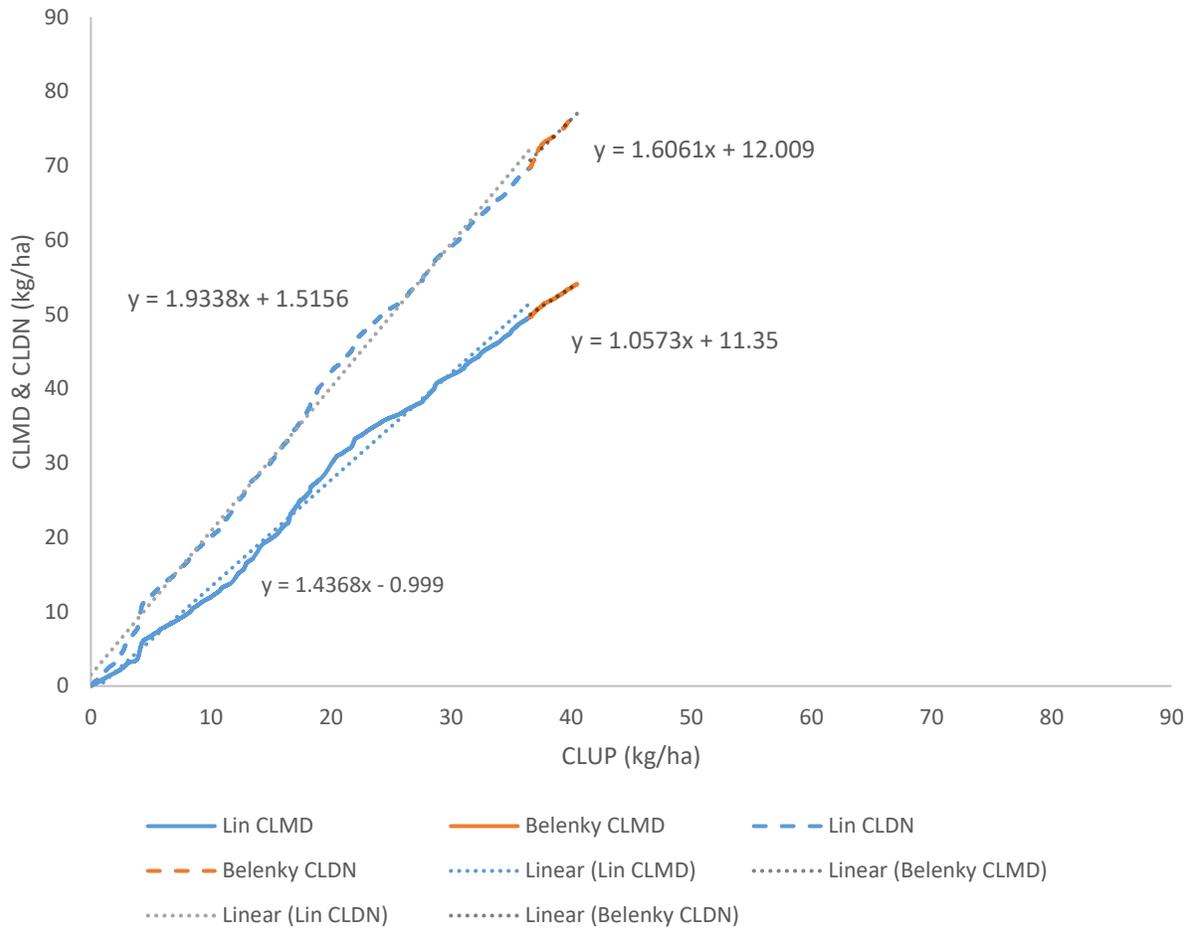


Figure 22. Cumulative DOC CLMD (solid) & CLDN (dashed) (kg/ha) vs. Cumulative DOC CLUP (kg/ha).

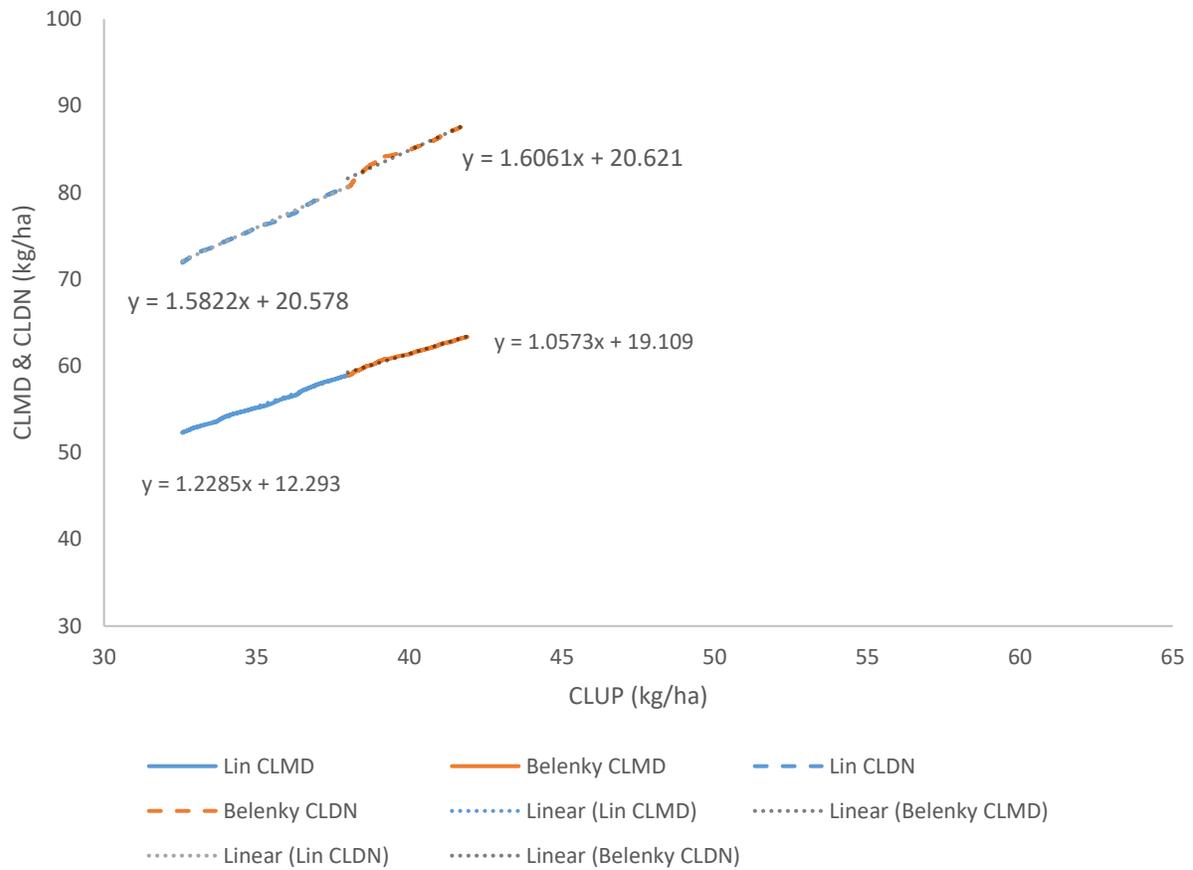


Figure 23. Cumulative DOC CLMD (solid) & CLDN (dashed) (kg/ha) vs. Cumulative DOC CLUP (kg/ha) using data from Lin (2017) from 18-01-2015 onward.

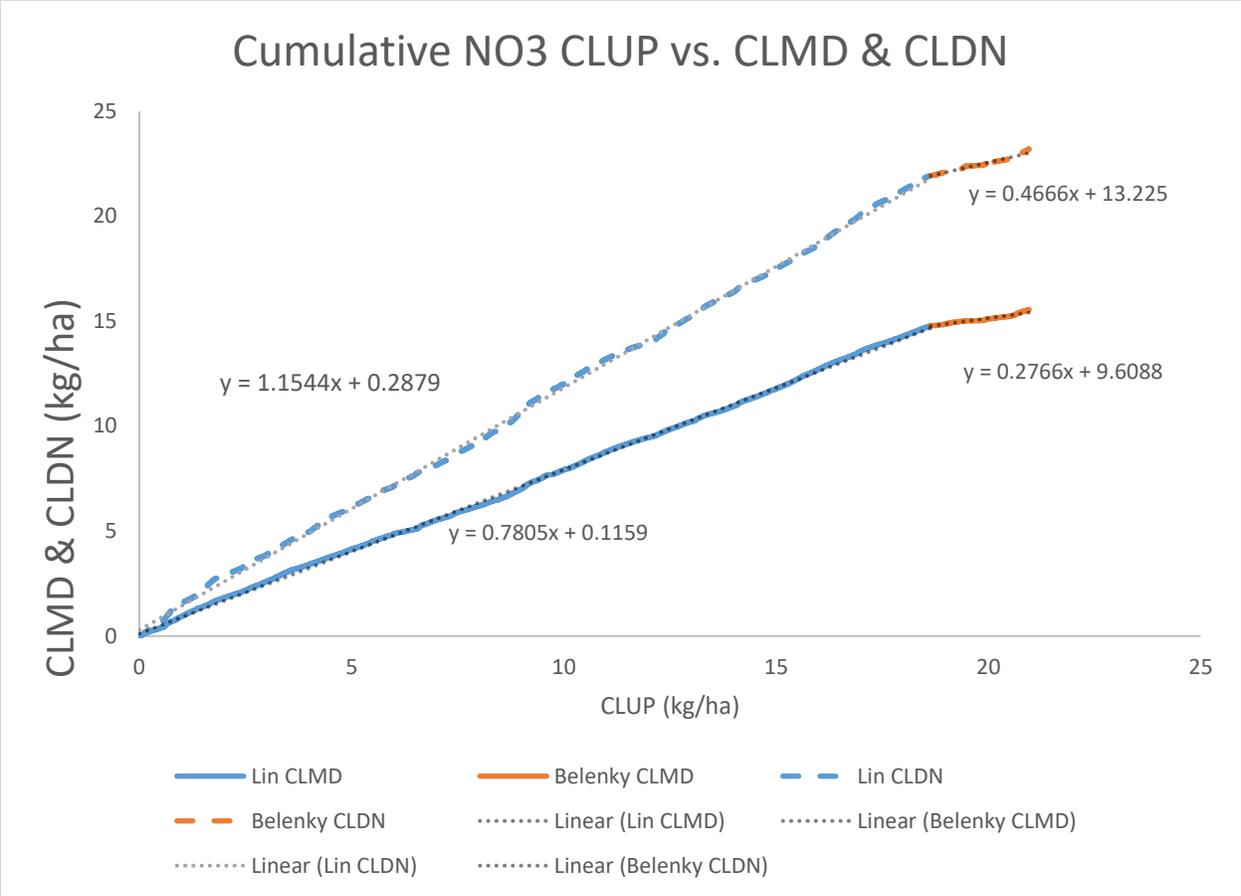


Figure 24. Cumulative nitrate CLMD (solid) & CLDN (dashed) (kg/ha) vs. cumulative nitrate CLUP (kg/ha) and one-to-one line (long dashed).

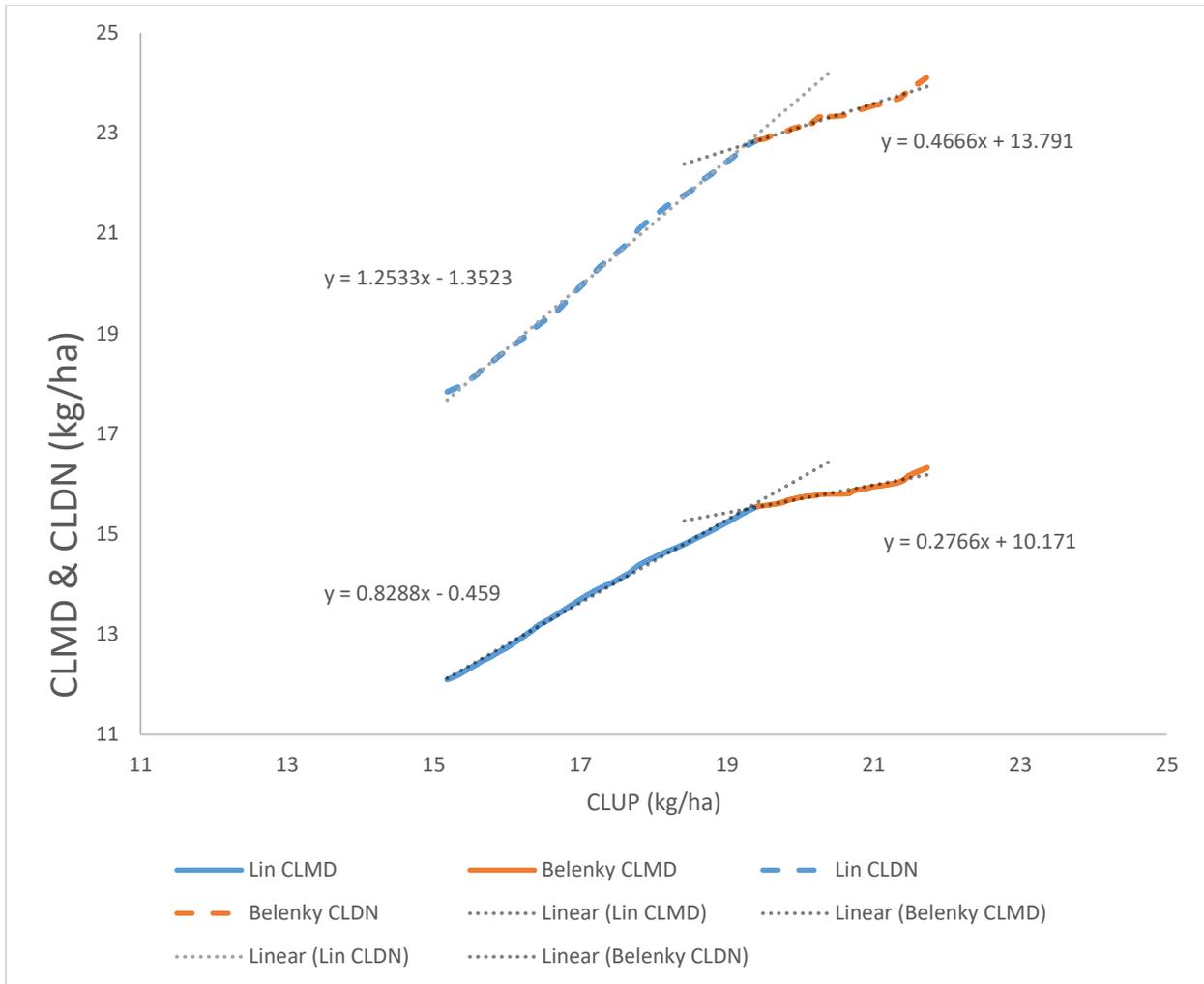


Figure 25. Cumulative nitrate CLMD (solid) & CLDN (dashed) (kg/ha) vs. cumulative nitrate CLUP (kg/ha) using data from Lin (2017) from 18-01-2015 onward and one-to-one line (long dashed).

Discussion of Possible Reasons for Apparent Relative Loading Changes between Stations

Possible land use/ land cover changes that might have occurred in the downtime between monitoring periods are a possible reason for the significant reduction. Results from CLUP show that the load-to-flow ratios for DOC and nitrate remain very similar pre- and post-restoration, indicating no significant changes in the export signature of sub-watershed I (Figure 5). Other than restoration and the by-pass, there are no obvious visible changes to sub-watersheds II and III. The controlled animal feeding operation (CAFO) in sub-watershed II and the farm and post-

processing facility in sub-watershed III were known to be active during monitoring, so there is no reason to suspect the nitrate addition from these sources had ceased.

In the same vein, we cannot rule out that the restoration was ineffective. The apportionment between the effect of possible land use changes (no obvious changes observed), and the effect of the restoration cannot be determined. However, it is possible to list all the potential effects of the restoration on water quality and identify any corresponding observations. The DOC removal processes in-stream include microbial respiration and algae and macrophyte assimilation. The DOC production processes include incomplete mineralization of both autochthonous and allochthonous organic matter, in the water column and the sediment. The latter corresponding to leaves and branches flowing from upstream into the restoration. Nitrate removal processes in-stream include macrophyte and algae uptake and denitrification by water column biofilms and in the sediment, while the nitrate producing processes include nitrification of ammonium resulting from the mineralization of the organic matter.

The restoration work which re-aligned the channel to be more sinuous and excavated a lower, more accessible floodplain resulted in a sand bottom channel, which provided an abundance of light for algae and macrophytes. The consequences of the new sandy bottom, compared to the previous 'muck' between CLUP and CLMD, suggests that DOC production due to sediment diagenetic processes were initially halted, at least immediately post-restoration, and likely limited afterwards, even though large allochthonous organic matter in the form of leaves from upstream of CLUP was observed to enter the restoration with time. This may partially explain the relative 22% decrease in DOC export at CLMD. However, the less organic substrate should be less conducive to benthic denitrification as well.

However, the increase in light entering the channel post-restoration allowed widespread establishment of invasive, non-native alligatorweed (*Alternanthera philoxeroides*), in low velocity areas across the entire channel. In higher velocity areas, macrophytic hummocks established supporting epiphytic algae within the channel. The increased presence of luxuriant aquatic vegetation compared to the pre-restoration canal likely played a role in nitrate uptake, especially during the warmer season from June to September 2017. It is also possible that the extra organic matter produced and trapped by the hummocks was in fact conducive to denitrification.

Additionally, increased local water velocities due to the minor in-stream blockages near the hummocks, might have increased hyporheic exchange (Francois Birgand, 2000; Findlay, 1995; Hill, 1988). Water directly in front of a hummock may be forced downward into the substrate and travel underneath the channel (Figure 26; longitudinal section), while water forced to flow around a hummock may enter the stream bank and join subsurface flow or in-stream flows (Figure 26; planar view).

Preliminary data from a comparison of two tracer studies conducted pre- and post-restoration suggested that there is increased transient storage within the reach, supporting the hypotheses that transient exchange (hyporheic plus water column storage in macrophytic mats) has increased between the two periods (Danielle Winter, personal communication).

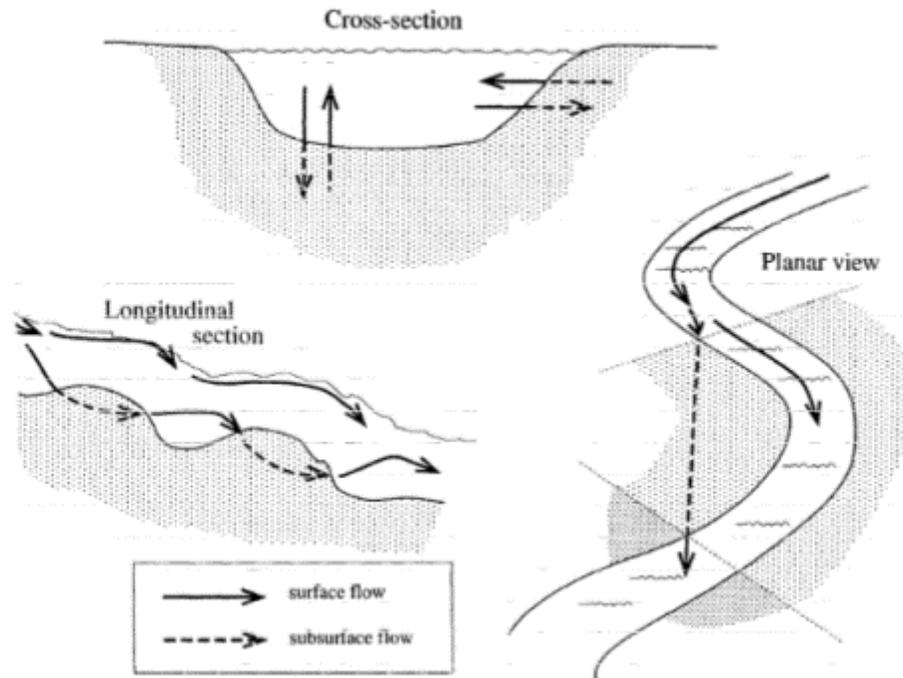


Figure 26. Diagram from Findlay (1994) demonstrating the exchange of water with the hyporheic zone in all three dimensions.

Major Visible Physical Effects of the Restoration

The excavation of the floodplain and the creation of the new more sinuous smaller channel has increased the linear length of stream by 20% from 2,206 m to 2,652 m (NEU, 2011). This increased the potential reactive surface area (banks and benthos) and possibly the residence time. The restoration also removed a large amount of vegetation that had been shading the Canal. Greater exposure to sunlight increases water temperatures, allowing for potentially increased microbial activity (Hill, 1988). The increase in light entering the channel post-restoration also allowed macrophytic hummocks to take root within the channel. Macrophytes facilitated a decrease of nitrate through generating biomass (Figure 27). Another possibility is that the restoration facilitated processes conducive to denitrification. The bacteria responsible for denitrification require (1) anaerobic conditions, (2) NO_3 to be denitrified, and (3) readily available source of organic carbon (Knowles, 1982).



Figure 27. Alligatorweed covering the channel during the summer.

The stream substrate, wetland conditions in tributaries, floodplain and riparian buffers of the restoration likely created anaerobic conditions needed for denitrification (Burt, Matchett, Goulding, Webster, & Haycock, 1999; Messer, Burchell, Grabow, & Osmond, 2012; Roley et al., 2012). The majority of in-stream microbial activity takes place within the first few millimeters of the stream substrate (Francois Birgand, 2000). The interface of the water column and the stream bottom is a mixture of aerobic and anaerobic environments that allow obligate oxic or anoxic biotic and abiotic processes to occur (Findlay, 1995). The earthmoving done during the restoration significantly altered the stream substrate. What was previously a “mucky” less permeable stream bottom heavy in organic matter is now a more permeable sandy substrate. The restoration abandoned the existing mucky incised channel and excavated a new smaller meandering channel through sandy alluvial deposits from the nearby Little River. The apparent consumption of DOC between CLUP and CLMD could be a result of the new stream bottom is potentially exporting DOC at a greatly reduced rate rather than consuming DOC at a vastly

greater rate. DOC is likely still being consumed. Any other assertion would assume many in-stream processes are no longer taking place, however it is difficult to apportion the amount of DOC being consumed or released to their respective processes. It is important to note that post-restoration the area immediately upstream of CLDN was visibly higher in organic matter relative to the remainder of the restoration, compared to the sandy soil further upstream. This last observation may explain why the DOC export at CLDN had apparently changed, although it decreased at CLMD. Some additional process had to compensate for the decrease in the upper part of the stream.

While the literature is divided as to which process can be credited with the majority of nitrate removal from streams, the nitrate reduction at the study site is due to some combination of biomass production and denitrification. Similarly, it is difficult to a priori apportion the apparent changes in DOC and nitrate dynamics to land use/land cover or in-stream processes, despite having observed no obvious land use/land cover changes within the nested watersheds. We have, however, been able to develop metrics to credit the restoration with measured changes.

Metrics for Crediting the Restoration for the Measured Effects

Hypothetical DOC and Nitrate Loading

Using the regression relationship established with the pre-restoration data, the hypothetical predicted mass of DOC and nitrate exported, assuming the restoration had not occurred, can be estimated. Based on the regression relationship established with the pre-restoration data, I was able to estimate the mass of DOC and nitrate exported had the restoration not taken place. As with the continuity analysis the predicted loads using the pre-restoration regressions created with data collected after 18-01-2015, see regression equations used for each station and parameter below.

	CLMD		
DOC:	$y = 1.2376 * x + 4.4607$	$R^2 = 0.9959$	(Equation 3)
NO3:	$y = 0.8105 * x - 0.2752$	$R^2 = 0.9970$	(Equation 4)

	CLDN		
DOC:	$y = 1.5933 * x + 11.545$	$R^2 = 0.9984$	(Equation 5)
NO3:	$y = 1.2674 * x - 1.5509$	$R^2 = 0.9979$	(Equation 6)

Variable x is the cumulative load at CLUP at the end of post-restoration monitoring

Using these equations, I predicted CLMD to export less DOC and nitrate, to an order of 345 (3,355 kg/year post vs 3,700 kg/year predicted) and 872 kg/year (584 kg/year post vs 1,455 kg/year predicted) less, respectively. At CLDN, measured DOC exceeded predicted DOC by 958 kg/year (7,541 kg/year post vs 6,584 kg/year predicted), while measured nitrate continued to be lower than the predicted values by 1,879 kg/year (1,318 kg/year post vs 3,197 kg/year predicted) (Table 13). These results indicate an increase in nitrate treatment through the reach and a reduction in DOC from sources between CLUP and CLMD. However, between CLMD and CLDN there appears to be a large source of DOC. We hypothesize that the wetland conditions at the end of the reach are the primary sources of this DOC.

Table 13. Annual mass of DOC and NO3 exported post-restoration compared to annual masses predicted using equations 3-6 in kg/yr.

	DOC (kg/yr.)			NO3 (kg/yr.)		
	Measured	Predicted	Difference	Measured	Predicted	Difference
CLUP	1695			1003		
CLMD	3355	3700	-345	583.5	1455	-872
CLDN	7541	6584	958	1318	3197	-1879

CLDN/CLUP DOC Relationship Gives Clues to the Restoration Influencing Nutrient Dynamics

DOC dynamics within the reach give us the first indicator that the restoration has an influence on nutrient dynamics. The CLUP-CLMD portion of the restoration, with its OM

deficient stream bottom and floodplain is retaining DOC while the area immediately upstream of CLDN still visibly rich in organic matter is still exporting DOC.

We hypothesized that DOC export is relatively higher at CLDN because of the large wetland that has established in the reach which is particularly conducive to production of DOC. For the first 2 months of monitoring the CLMD-CLDN region exported high amounts of DOC relative to what is entering CLUP (slope of 2.85 over 76 days; Figure 28). This may be due to the production of autochthonous DOC during the summer months, however the data appear inconsistent and we suspect either probe error or erratic nutrient inputs from the tributary that drains a produce post-processing facility. Following this period there was a large storm event (01-09-2017 – 02-09-2017) that delivered inflow from the Little River. Though this event did not damage equipment, stations CLMD and CLDN only captured the event with discrete samples. Work to repair the damages from hurricane Matthew was conducted before and after the large rain event at the beginning of December. The repair work does not show a discernable impact on the nutrient dynamics of the reach.

Two interesting things happen after the December ‘resetting’ event. First, the stage (50th percentile 238 mm) at CLDN, which had been steadily decreasing between storm events, rose to a steady level (50th percentile 463 mm), indicating some form of downstream control. This increase in water level inundated the flood plain at least 70 m upstream of CLDN creating ideal anaerobic conditions conducive to DOC release. The relative export between CLUP and CLDN for this high stage period was 1.66. This is lower than before the storm, however, greatly reduced velocities were measured as result of the downstream control. The restoration has had a measurable effect on DOC dynamics by creating sinks and exposing sources, however the amount apportioned to each individual process cannot be determined. If the restoration

influenced DOC dynamics, then it is reasonable to conclude that it would also have an effect on nitrate dynamics.

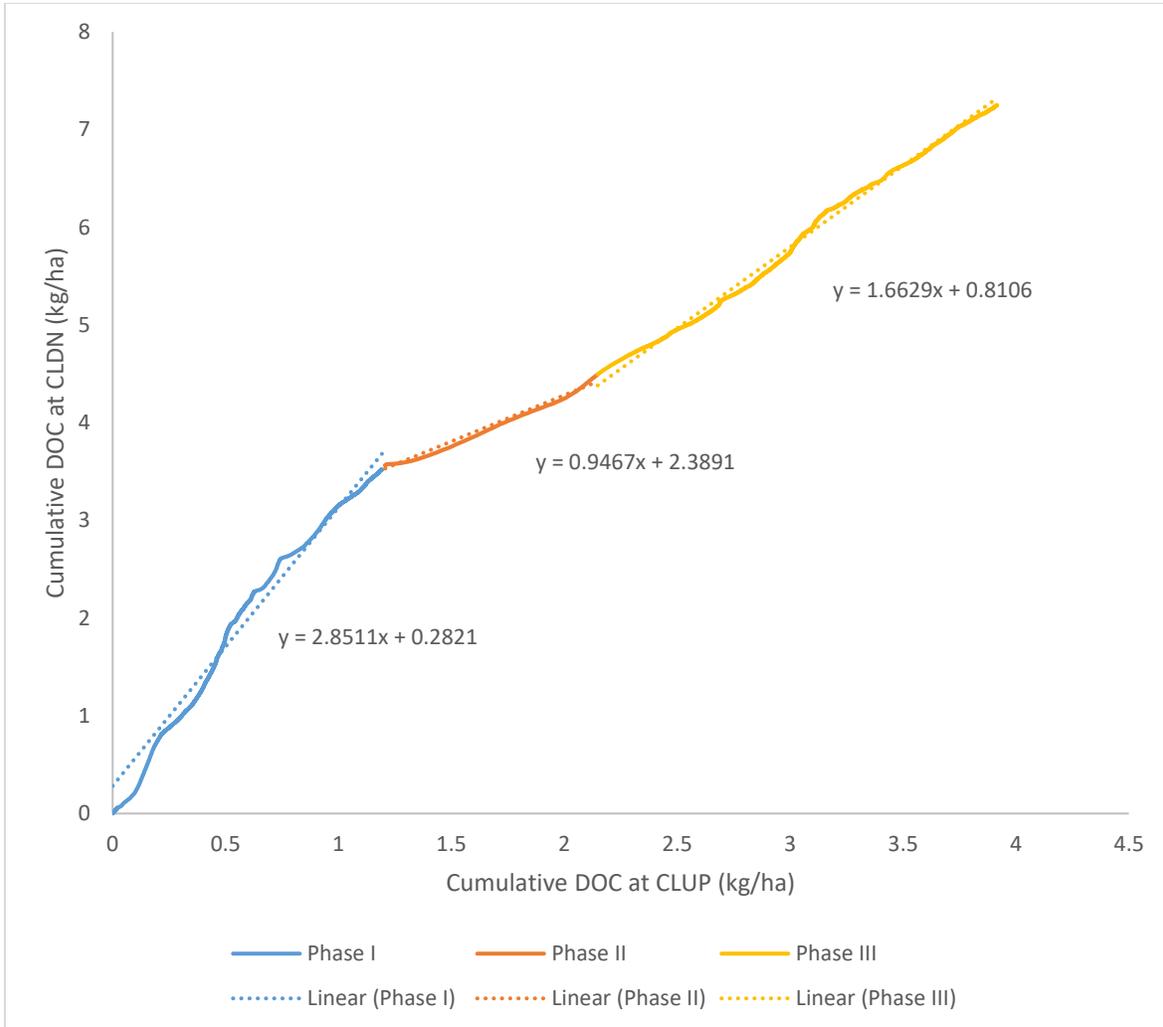


Figure 28. Post-restoration DOC CLDN vs CLUP in three distinct phases; Phase I (blue), Phase II (orange), Phase III (yellow).

Nitrate Treatment within the Reach Relative to Stream and Flood Prone Area

The second metric used to scale the changes in export values to project surface areas corresponds to the 50th percentile stage (A_{50}) and to bankfull stage (A_{bkf}) according to the plan drawings (NEU, 2011). In addition, the approximate flood prone area (A_{FP}) of the restoration was also calculated in order to include the two tributaries that were not counted towards the total stream length (Table 14).

Table 14. Stream properties used to calculate nutrient reduction metrics (NEU, 2011).

	Total/Mean	CLUP to CLMD	CLUP to CLDN	CLMD to CLDN
Stream length (m)	2652	1677 (63%)	2652	974 (37%)
Width of flood prone area (m)	19.20	-	-	-
Mean bankfull width (m)	4.08	-	-	-
Width at 50 th percentile of stage (m)	3.34	-	-	-
Stream area at bankfull (m ²)	10832	6850	10832	3982
Stream area at 50 th percentile of stage (m ²)	8858	5602	8858	3256
Flood prone area (m ²)	50918	32203	50918	18715

From CLUP to CLMD the relative nitrate reduction was 426, 349, and 50 mg/m²/day for A₅₀, A_{bkf} and A_{FP}, respectively. For the total length of the restoration, CLUP to CLDN, the reductions were 581, 475, and 78 mg/m²/day for A₅₀, A_{bkf} and A_{FP}. To determine the reductions for CLMD to CLDN, we took the difference of the two metrics just mentioned and determined that the restoration reduced nitrate by 155, 127, and 27 mg/m²/day for A₅₀, A_{bkf} and A_{FP} in the latter portion. These are significant relative reductions in nitrate as the typical reductions found for agricultural canals in the lower coastal plain are between 200-800 mg/m²/day (Francois Birgand, 2000). Even considering a maximum reduction in an agricultural canal (800 NO₃-N mg/m²/day) and the minimum reduction determined for the restoration canal (155 NO₃-N mg/m²/day), this is still a 19% decrease in nitrate. Reduction during channel flow and floodplain flow were not differentiated.

Table 15. Normalized apparent restoration effect in mg/m²/day for DOC and NO₃ and the percentage of total change in NO₃ and percentage of total area corresponding to each change (*per m² of floodprone area includes the approximate areas of UT1 and UT2).

	DOC (mg/m ² /day)	NO ₃ (mg/m ² /day)	% change of total NO ₃	% of total area
CLUP to CLMD				
Stream area at 50th percentile stage	-168.9	-426.3	73.3 %	63.2 %
Stream area at mean bankfull stage	-138.1	-348.6	73.3 %	63.2 %
Per m ² of floodprone area*	-19.9	-50.2	64.6 %	71.8 %
CLMD to CLDN				
Stream area at 50th percentile stage	465.1	-155.0	26.7 %	36.8 %
Stream area at mean bankfull stage	380.3	-126.7	26.7 %	36.8 %
Per m ² of floodprone area*	59.5	-27.48	35.4 %	28.2 %
CLUP to CLDN				
Stream area at 50th percentile stage	269.2	-581.3	-	-
Stream area at mean bankfull stage	242.2	-475.4	-	-
Per m ² of floodprone area*	39.6	-77.7	-	-

The portion of the restoration that lies between CLUP and CLMD is roughly 63% of the restored stream with the remaining 37% being between CLMD and CLDN. It is interesting to note that the reduction in nitrate for the first section is approximately 73% and 27% for the second portion. The proportions are therefore not the same, with apparently more relative removal between CLUP and CLMD, than CLMD to CLDN. This may be due to the observed large additions of sand due to UT3, 200 m downstream of CLMD, which has visibly filled the channel and prevented vegetation from establishing. This suggests that the wetland area just upstream of CLDN was particularly efficient at stripping nitrate, enough so to compensate the lack of vegetation immediately after UT3. In terms of flood prone area, which included the two tributaries, the proportions were 72% between CLUP and CLMD and 28% between CLMD and

CLDN, which is closer to the apparent nitrate reduction apportionment observed (Table 15). This may indicate that the transformation of tributaries into wetlands played an important role.

Using the flood prone area as a basis to calculate reduction proportions provides a close match. While the individual processes responsible for the relative removal of nitrate from the reach cannot be pinpointed, this relationship of length and especially area to apparent nitrate removal strongly suggest the processes are native to the reach. Therefore, based on the processes observed visually combined with the measured loads within the restoration, there is sufficient coincidental evidence that the restoration is responsible for a significant inflection observed in the double mass curves. Barring some major yet undiscovered land use change, the data suggests that the stream restoration provided large water quality benefits during a period of relatively low flow.

1.6 Conclusions

During the first year of post-restoration monitoring it was possible to continue monitoring on site and significantly improve the quantity and quality of data collected by elevating the monitoring stations above the terrace floodplain, providing local power generation and storage for all equipment, reducing power consumption and simplifying spectrophotometer sampling and cleaning. Using the techniques developed during pre-restoration monitoring it was possible to establish good correlations for two of seven target parameters, DOC and Nitrate, by applying PLSR to high-frequency spectrophotometry data and discrete samples. The predicted concentrations from PLSR matched the behavior known for their respective parameters. Future regressions would benefit from a greater range of concentration samples as recommended by Lin (2017). While the total rainfall depth between the two monitoring periods differed, the inlet/outlet relationship between the reference and the treatment stations remained constant

allowing the research to move forward and quantify the changes in water quality through the reach. For DOC and nitrate, it was possible to quantify the magnitude and direction of the change for the first-year post-restoration.

It is important to note that this is not the denitrification potential, or the total amount of DOC or nitrate retained per year, only the change from the conditions present in the pre-restoration agricultural canal. The nitrate reductions in each section of The Canal were approximately proportional to the length of each section and to a greater degree with the respective flood prone areas. This strongly suggests that the increased treatment is a result of the restoration and not land use or climatic changes.

1.7 Considerations for Future Work

Basic Inlet/Outlet Sampling for UT 1 and UT2

Qianyu Hang began collecting grab samples at outlets of all tributaries to the restoration in 2018. Going forward, inlet grab samples will allow rudimentary treatment capacities of the tributaries to be quantified. Coupled with flow monitoring in the form of V-notched weirs and a device to measure head above the weir, this will also allow incoming and outgoing loads to be calculated.

Hurricane/Event Sampling

Lin et al. (2017) as well as this study witnessed large portions of the cumulative load curves resulting from a single rain event. Phase II shown in Figure 28, makes up approximately one sixth of the cumulative DOC loading during the post-restoration monitoring period and only lasted for two days. Because of the large loads that can be carried through the restoration during such events, it would be beneficial to sample at a higher rate during larger events using a secondary discrete sampler set to trigger with a sudden increase in stage or similar criteria.

Collecting additional discrete samples would also help stratifying sampling over a range of concentration values, shown to be good for PLSR calibration (Lin, 2017).

REFERENCES

- Andréassian, V., Parent, E., & Michel, C. (2003). A distribution-free test to detect gradual changes in watershed behavior. *Water Resour. Res.*, 39(9).
- Aquatic Information Inc. (2009). Aquarius Hydrologic Workstation Software. Water St., Vancouver, B.C. V6B 1B6, Canada. Retrieved from info@aquaticinformatics.com
- Bernhardt, E. S., Palmer, M. A., Allan, J. D., Alexander, G., Barnas, K., Brooks, S., ... Sudduth, E. (2005). Ecology - Synthesizing {US} river restoration efforts. *Science*, 308(5722), 636–637.
- Birgand, F. (2000). Quantification and Modeling of {In-Stream} Processes in Agricultural canals of the lower coastal plain. *Hydrology*.
- Birgand, F., Appelboom, T. W., Chescheir, G. M., & Skaggs, R. W. (2011). Estimating nitrogen, phosphorus, and carbon fluxes in forested and mixed-use watersheds of the lower coastal plain of North Carolina: Uncertainties associated with infrequent sampling. *Transactions of the ASABE*, 54(6), 2099–2110.
- Birgand, F., Benoist, J. C., Novince, E., Gilliet, N., Cast, P. Saint, & Saos, E. Le. (2005). Mesure des débits à l'aide de débitmètres ultrasoniques Doppler. Cas des petits cours d'eau ruraux. *Ingénieries - E A T*, (41), 23–38. Retrieved from <https://hal.archives-ouvertes.fr/hal-00476108/>
- Birgand, F., Howden, N., Burt, T., & Worrall, F. (2017). Integrated indicators are important metrics of catchment biogeochemical function. *American Geophysical Union, Fall Meeting 2017, Abstract #H41F-1514*. Retrieved from <http://adsabs.harvard.edu/abs/2017AGUFM.H41F1514H>
- Birgand, F., Lellouche, G., & Appelboom, T. W. (2013). Measuring flow in non-ideal conditions for short-term projects: Uncertainties associated with the use of stage-discharge rating curves. *Journal of Hydrology*. <https://doi.org/10.1016/j.jhydrol.2013.09.007>
- Bosch, J. M., & Hewlett, J. D. (1982). A review of catchment experiments to determine the effect of vegetation changes on water yield and evapotranspiration. *J. Hydrol.*, 55(1), 3–23.
- Burt, T. P., Matchett, L. S., Goulding, K. W. T., Webster, C. P., & Haycock, N. E. (1999). Denitrification in riparian buffer zones: the role of floodplain hydrology. *Hydrological Processes*, 13(10), 1451–1463. [https://doi.org/10.1002/\(SICI\)1099-1085\(199907\)13:10<1451::AID-HYP822>3.0.CO;2-W](https://doi.org/10.1002/(SICI)1099-1085(199907)13:10<1451::AID-HYP822>3.0.CO;2-W)
- Colangelo, D. J. (2014). Interim response of dissolved oxygen to reestablished flow in the Kissimmee River, Florida, {USA}. *Restor. Ecol.*, 22(3), 376–387.
- Doll, B., Grabow, G. L., Hall, K., Halley, J., Harman, W., Jennings, G., & Wise, D. (2003). *Stream Restoration*. Retrieved from <https://semspub.epa.gov/work/01/554360.pdf>
- EPA. (2008). Clean Water Act. *EPA's Office*.
- Etheridge, J. R., Birgand, F., Burchell, M. R., & Smith, B. T. (2013). Addressing the fouling of in situ ultraviolet-visual spectrometers used to continuously monitor water quality in

- brackish tidal marsh waters. *J. Environ. Qual.*, 42(6), 1896–1901.
- Etheridge, J. R., Birgand, F., Osborne, J. A., Osburn, C. L., Burchell, M. R., & Irving, J. (2014). Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh. *LIMNOLOGY AND OCEANOGRAPHY-METHODS*, 12, 10–22.
- Findlay, S. (1995). Importance of surface-subsurface exchange in stream ecosystems: The hyporheic zone. *Limnology and Oceanography*, 40(1), 159–164. <https://doi.org/10.4319/lo.1995.40.1.0159>
- Flemming, H.-C. (2011). Microbial Biofouling: Unsolved Problems, Insufficient Approaches, and Possible Solutions (pp. 81–109). https://doi.org/10.1007/978-3-642-19940-0_5
- Hill, A. R. (1988). Factors influencing nitrate depletion in a rural stream. *Hydrobiologia*, 160(2), 111–122. <https://doi.org/10.1007/BF00015474>
- Hornbeck, J. W., Adams, M. B., Corbett, E. S., Verry, E. S., & Lynch, J. A. (1993). Long-term impacts of forest treatments on water yield: a summary for northeastern {USA}. *J. Hydrol.*, 150(2), 323–344.
- Howden, N., Birgand, F., Burt, T., & Worrall, F. (2018). Identifying trends in hydrological data: using integrated indicators to identify non-stationary behaviour. *Geophysical Research Abstracts EGU General Assembly, 20*, 2018–16128. Retrieved from <https://meetingorganizer.copernicus.org/EGU2018/EGU2018-16128.pdf>
- Howson, T. J., Robson, B. J., & Mitchell, B. D. (2009). Fish assemblage response to rehabilitation of a sand-slugged lowland river. *River Res. Appl.*, 25(10), 1251–1267.
- ISO 15769. (2010). ISO 15769 Hydrometry - Guidelines for the application of acoustic velocity meters using the Doppler and echo correlation methods.
- ISO 748. (1997). Measurement of liquid flow in open channel - Velocity-area methods. *International Standard*.
- Kenney, M. A., Wilcock, P. R., Hobbs, B. F., Flores, N. E., & Martinez, D. C. (2012). Is Urban Stream Restoration Worth It? *JAWRA Journal of the American Water Resources Association*, 48(3), 603–615.
- Kirchner, J. W., Feng, X., Neal, C., & Robson, A. J. (2004). The fine structure of water-quality dynamics: the (high-frequency) wave of the future. *Hydrol. Process.*, 18(7), 1353–1359.
- Knowles, R. (1982). Denitrification. *Microbiological Reviews*. Retrieved from <https://www.ncbi.nlm.nih.gov/pmc/articles/pmc373209/>
- Lepot, M., Torres, A., Hofer, T., Caradot, N., Gruber, G., Aubin, J.-B., & Bertrand-Krajewski, J.-L. (2016). Calibration of {UV/Vis} spectrophotometers: A review and comparison of different methods to estimate {TSS} and total and dissolved {COD} concentrations in sewers, {WWTPs} and rivers. *Water Res.*, 101, 519–534.
- Lin, C.-W. (2017, May). *Characterization of the Solute Dynamics Signature of an Agricultural Coastal Plain Stream, North Carolina, {USA}*. (F. Birgand, Ed.). North Carolina State

University.

- Marsh-McBirney Inc. (1990). *Marsh-McBirney, Inc. Flo-Mate Model 2000 Portable Flowmeter Instruction Manual*. Retrieved from https://www.hachflow.com/pdf/Model_2000_Manual.pdf
- Messer, T. L., Burchell, M. R., Grabow, G. L., & Osmond, D. L. (2012). Groundwater nitrate reductions within upstream and downstream sections of a riparian buffer. *Ecological Engineering*, 47, 297–307. <https://doi.org/10.1016/J.ECOLENG.2012.06.017>
- Morandi, B., Piégay, H., Lamouroux, N., & Vaudor, L. (2014). How is success or failure in river restoration projects evaluated? Feedback from French restoration projects. *J. Environ. Manage.*, 137, 178–188.
- Morlock, S., Nguyen, H., & Ross, J. (2002). *Feasibility of acoustic Doppler velocity meters for the production of discharge records from US Geological Survey streamflow-gaging stations*. Retrieved from http://www.commtec.com/library/Technical_Papers/USGS/advm.pdf
- NEU. (2011). *On-site Stream Mitigation Plan for {US} Highway 70 Goldsboro Bypass Construction*.
- Palmer, M., Allan, J. D., Meyer, J., & Bernhardt, E. S. (2007). River Restoration in the Twenty-First Century: Data and Experiential Knowledge to Inform Future Efforts. *Restoration Ecology*, 15(3), 472–481. <https://doi.org/10.1111/j.1526-100X.2007.00243.x>
- R Core Team. (2017). *R: A Language and Environment for Statistical Computing*. Vienna, Austria. Retrieved from <https://www.r-project.org>
- Ritter, A., & Muñoz-Carpena, R. (2013). Performance evaluation of hydrological models: Statistical significance for reducing subjectivity in goodness-of-fit assessments. *Journal of Hydrology*, 480, 33–45. <https://doi.org/10.1016/J.JHYDROL.2012.12.004>
- Robinson, & Chamberlain. (1960). Trapezoidal Flumes for Open-Channel Flow Measurement. *Transactions of the ASAE*, 3(2), 0120–0124. <https://doi.org/10.13031/2013.41138>
- Roley, S. S., Tank, J. L., Stephen, M. L., Johnson, L. T., Beaulieu, J. J., & Witter, J. D. (2012). Floodplain restoration enhances denitrification and reach-scale nitrogen removal in an agricultural stream. *Ecological Applications*, 22(1), 281–297. <https://doi.org/10.1890/11-0381.1>
- Rosgen, D. (1994). *A Classification of Natural Rivers*. Retrieved from http://www.science.earthjay.com/instruction/HSU/2016_fall/GEOL_332/labs/lab_04/Rosgen_1994_Classification_Rivers.pdf
- SonTek/YSI. (2011). *White Paper: Product Introduction - The SonTek-IQ*. Retrieved from www.sontek.com/iq
- SonTek. (2015). *TECH NOTE: SonTek-IQ Index Velocity Classification*. Retrieved from <https://www.sontek.com/media/pdfs/sontek-iq-index-velocity-classification.pdf>
- Stednick, J. D. (1996). Monitoring the effects of timber harvest on annual water yield. *J. Hydrol.*,

176(1), 79–95.

USACE, & EPA. (n.d.). *Proposed Compensatory Mitigation Rule: Improving, Restoring, and Protecting the Nation's Wetlands and Streams*.

USGS. (2011). StreamStats. Retrieved from <https://streamstats.usgs.gov/ss/>

Whelan, A., Monitoring, F. R.-J. of E., & 2006, undefined. (n.d.). Antifouling strategies for marine and riverine sensors. *Pubs.Rsc.OrgPaperpile*. Retrieved from <http://pubs.rsc.org/-/content/articlehtml/2006/em/b603289c>

Wortley, L., Hero, J.-M., & Howes, M. (2013). Evaluating Ecological Restoration Success: A Review of the Literature. <https://doi.org/10.1111/rec.12028>

APPENDICES

Appendix A: PLSR Calibration Plots

The following section contains all plots generated during the PLSR calibration for all seven parameters. The left column contains the regressions for the spring/summer period and the right column contains the fall/winter regressions. The three rows of plots between captions always correspond to CLUP, CLMD and CLDN.

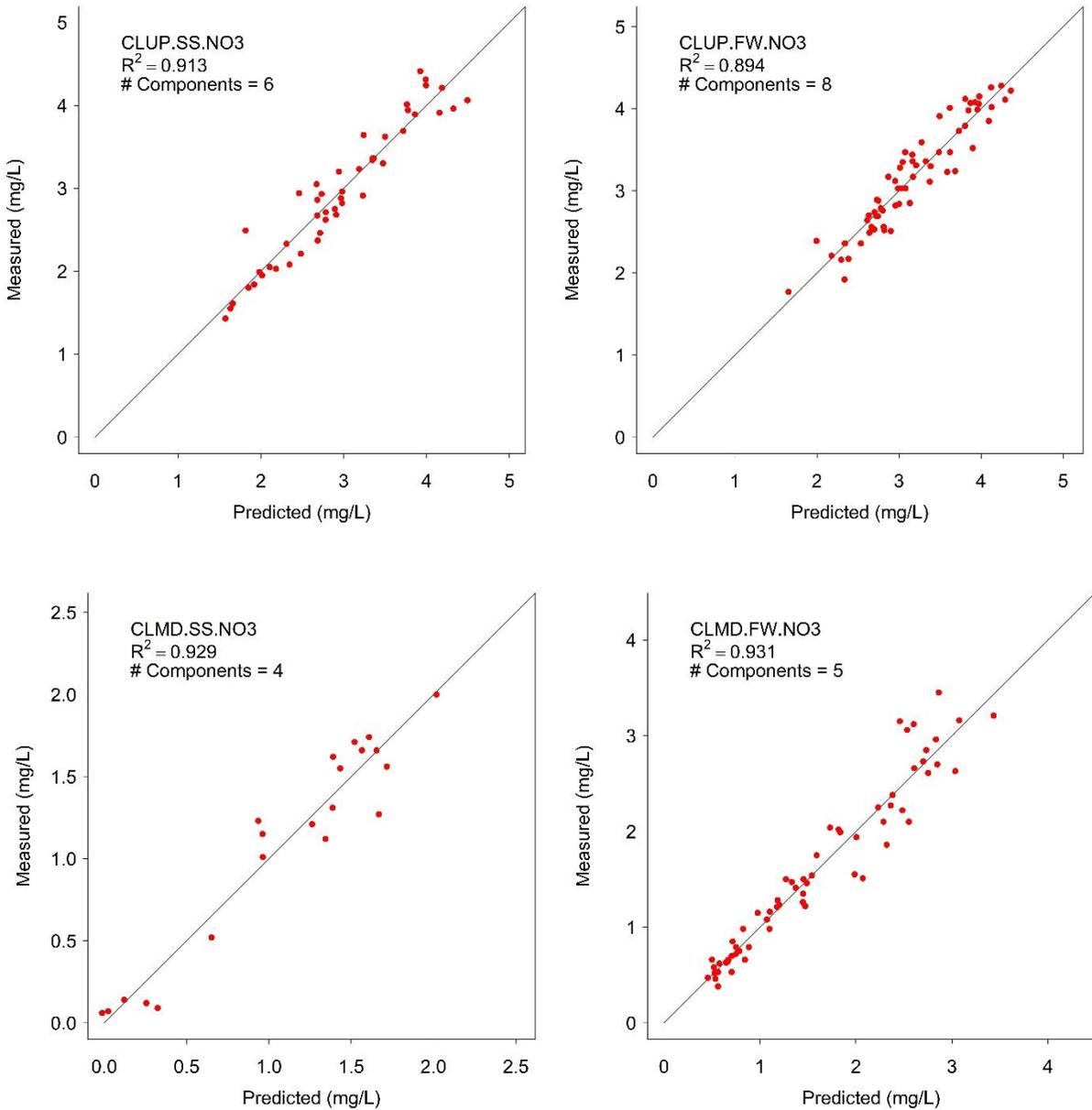


Figure A1. Regression relationships between measured nitrate concentrations from discrete sampling and predicted nitrate concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).

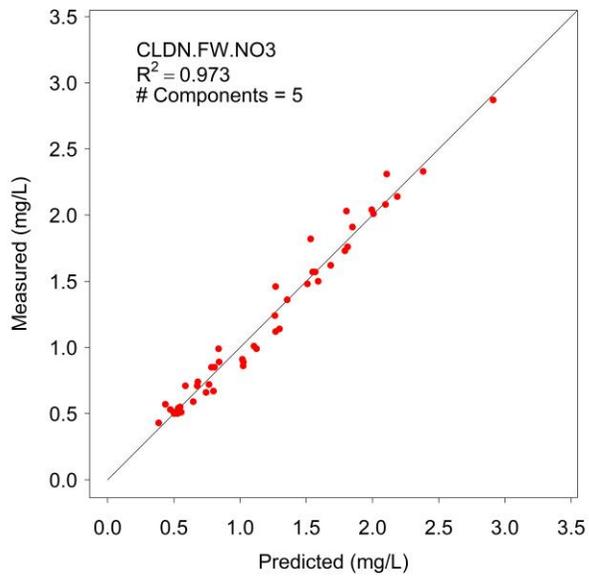
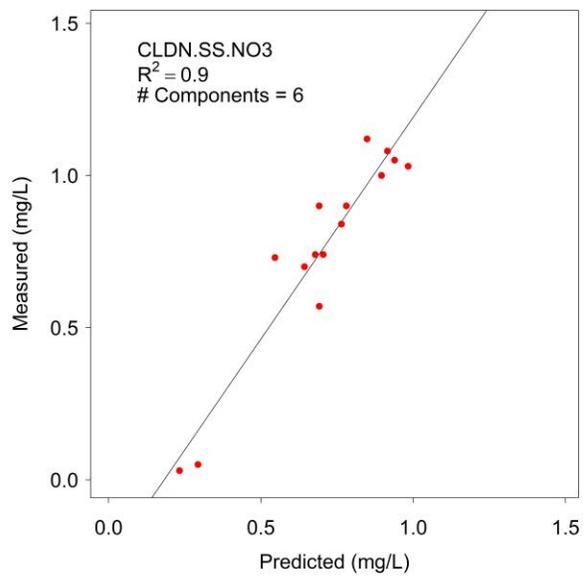


Figure A1. (continued).

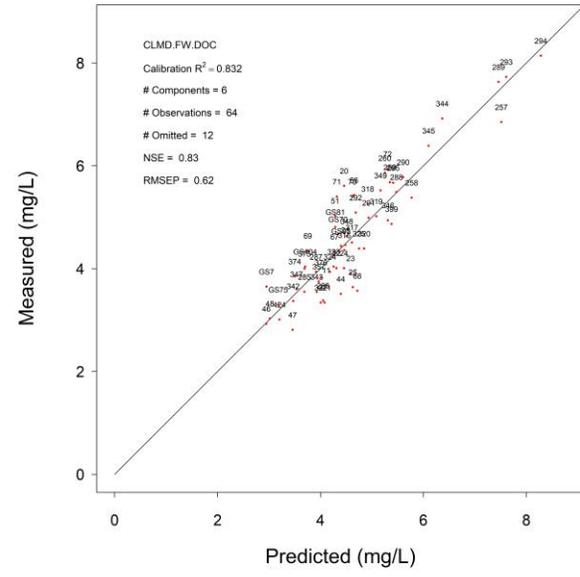
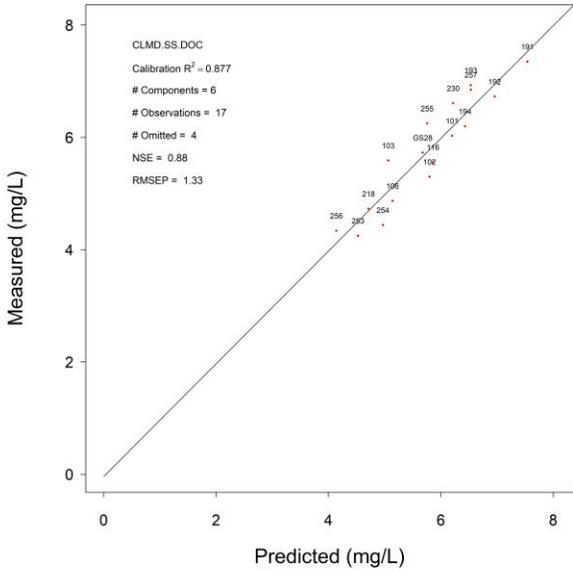
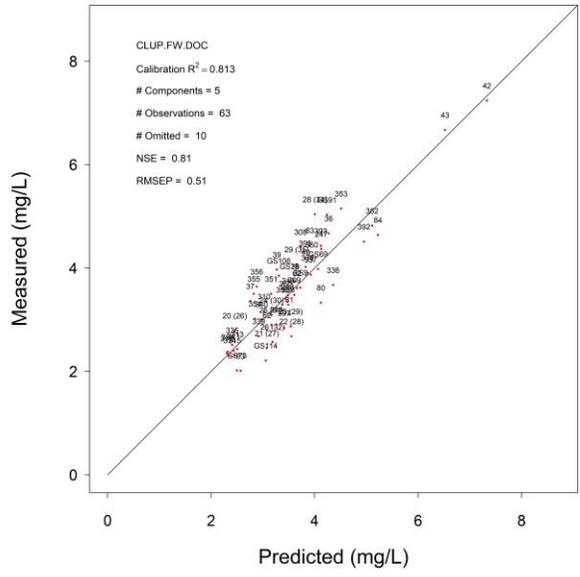
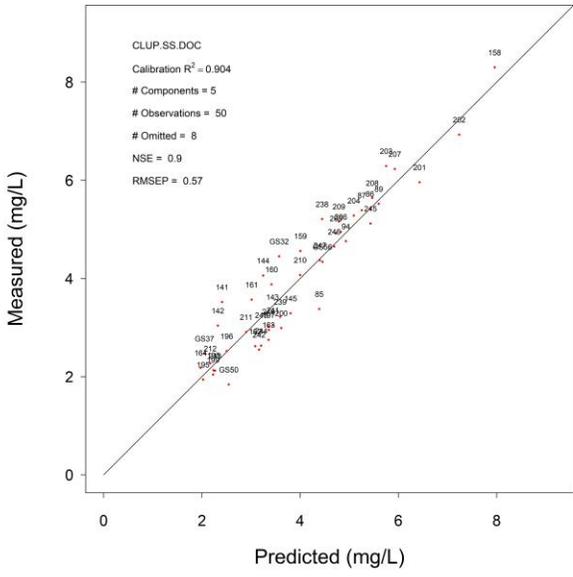


Figure A2. Regression relationships between measured DOC concentrations from discrete sampling and predicted DOC concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).

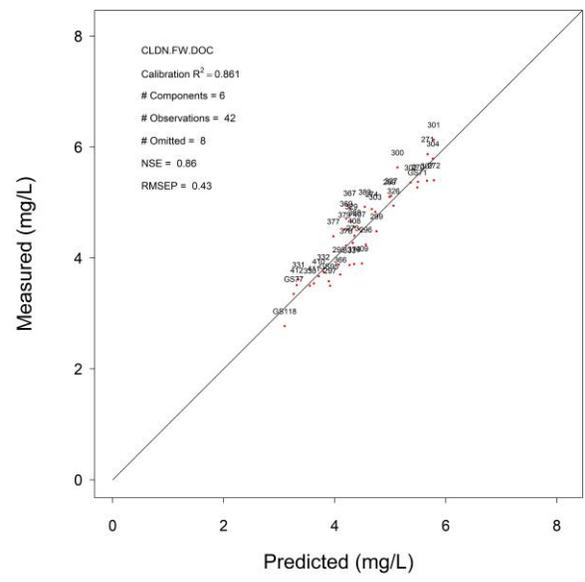
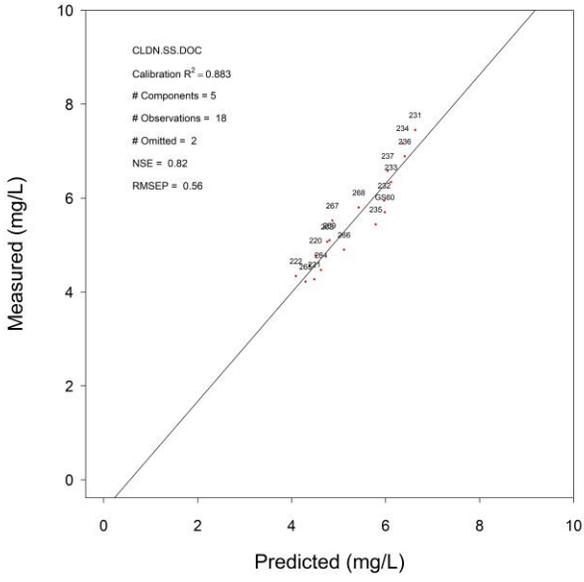


Figure A2. (continued).

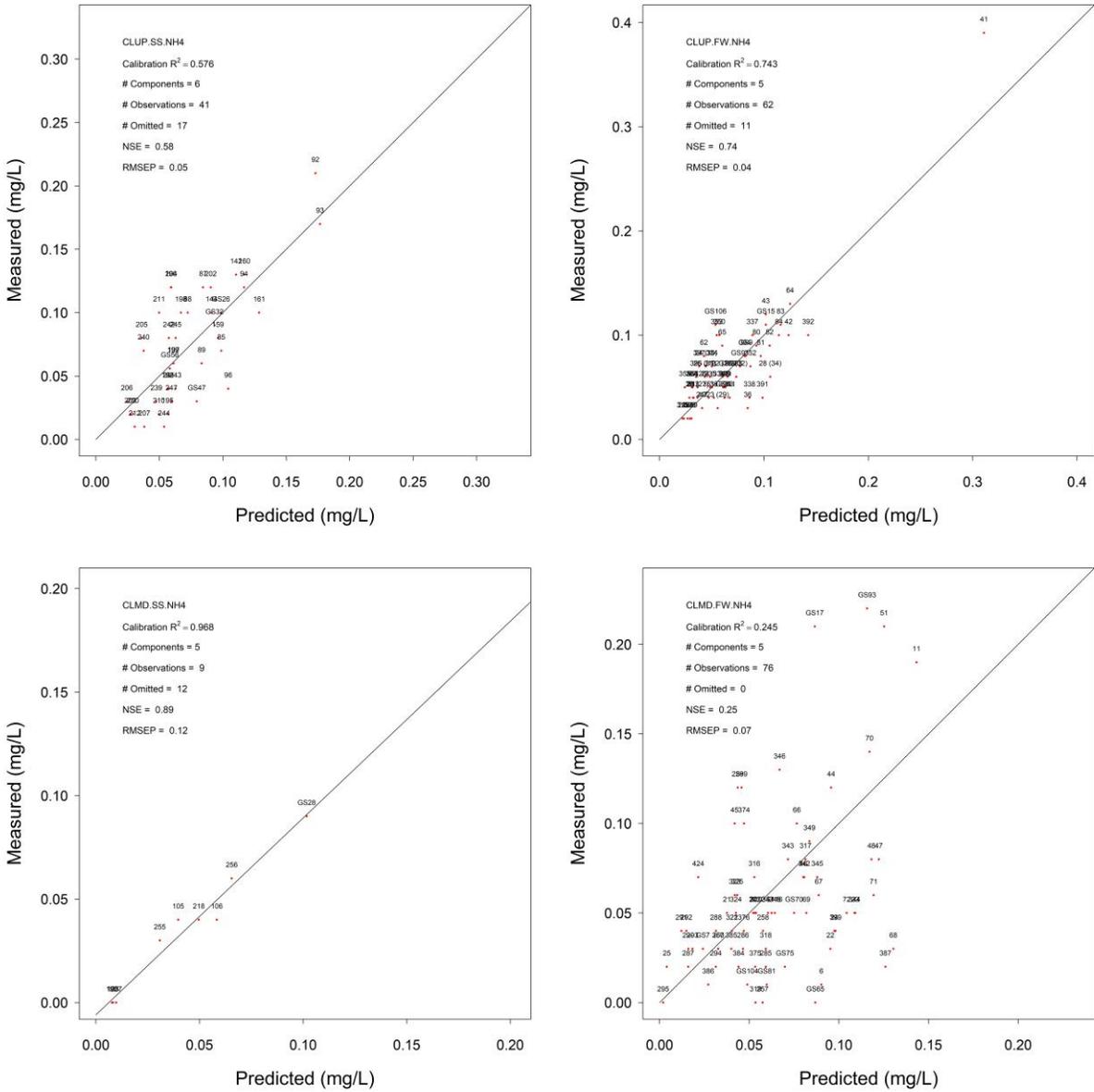


Figure A3. Regression relationships between measured ammonium concentrations from discrete sampling and predicted ammonium concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).

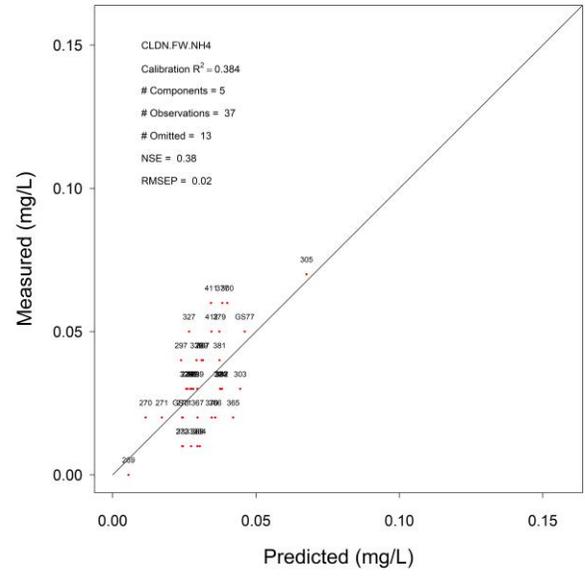
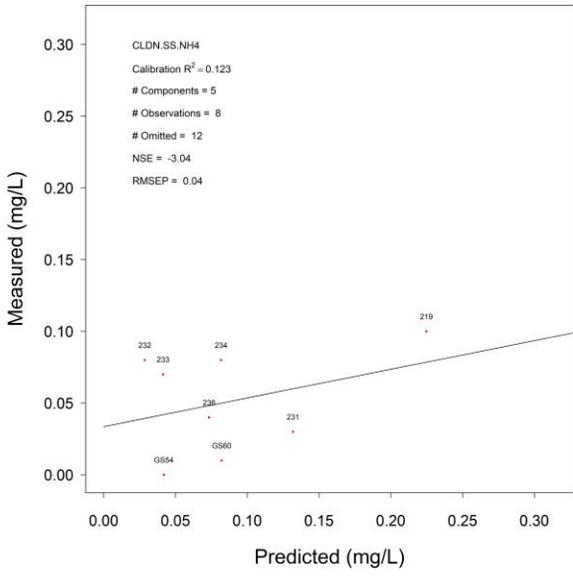


Figure A3. (continued).

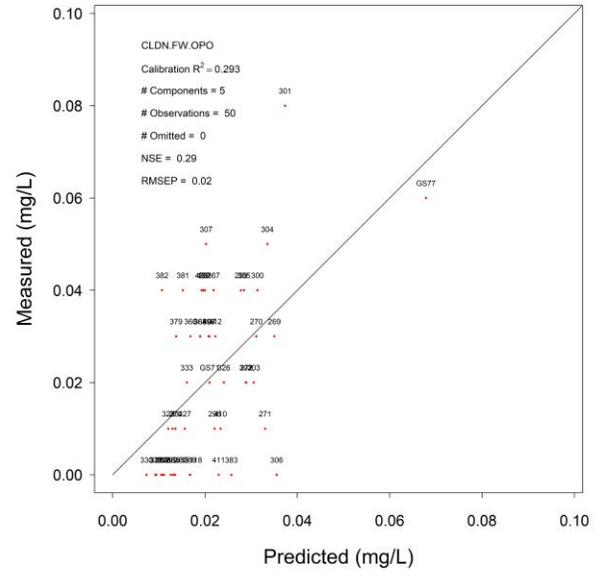
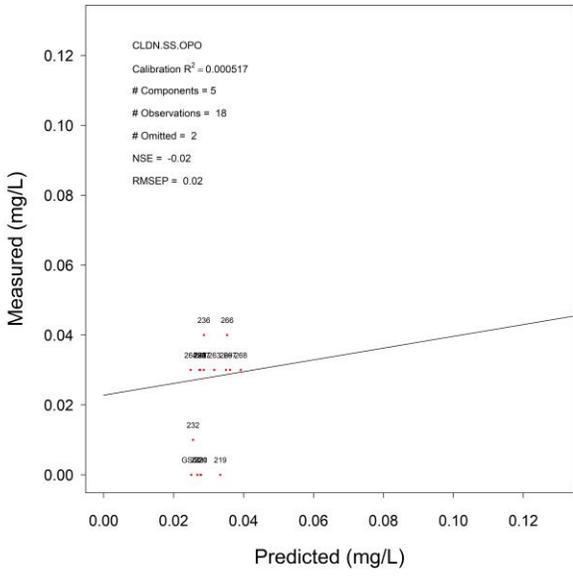


Figure A4. (continued).

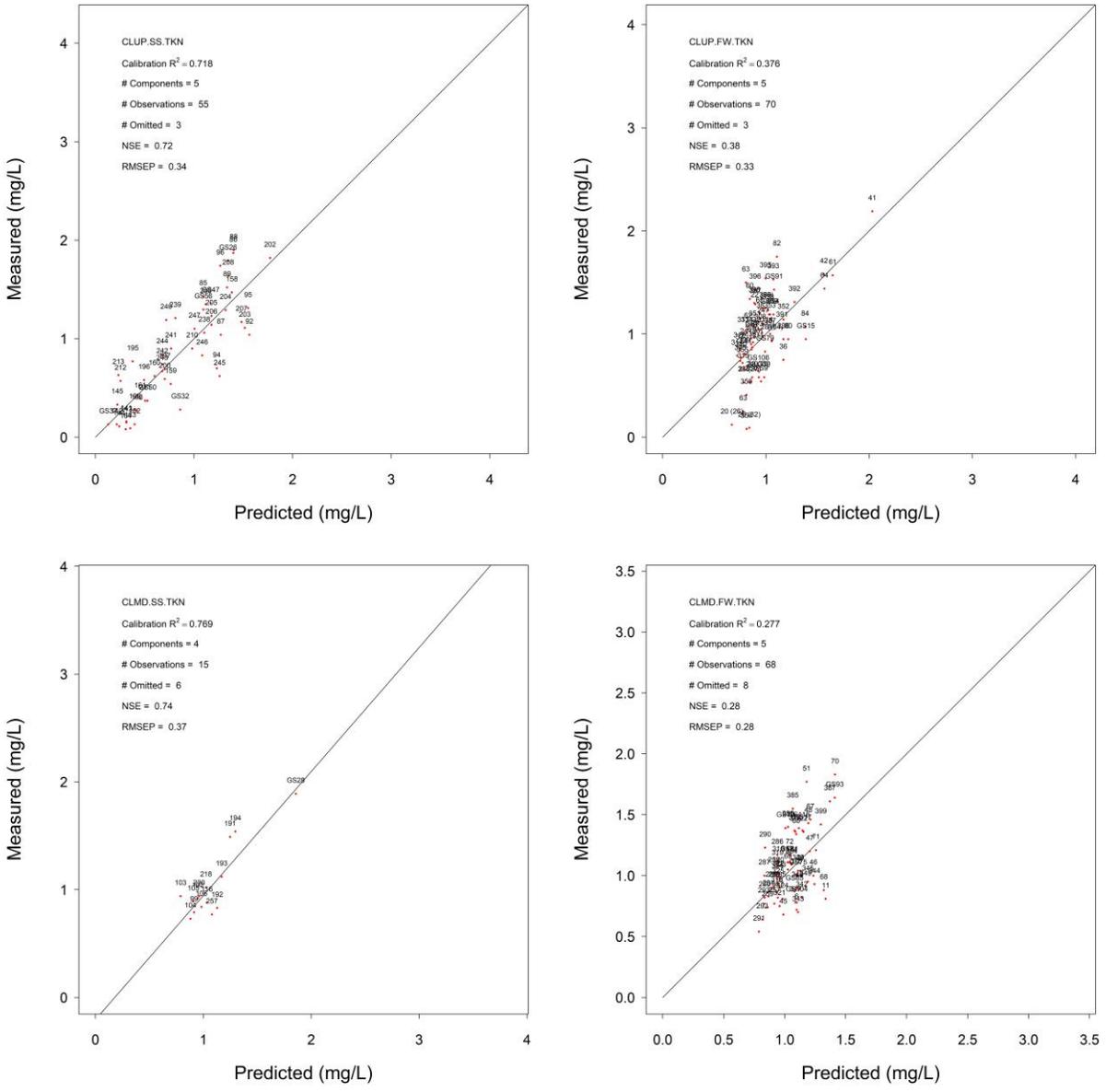


Figure A5. Regression relationships between measured total kjeldahl nitrogen concentrations from discrete sampling and predicted total kjeldahl nitrogen concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).

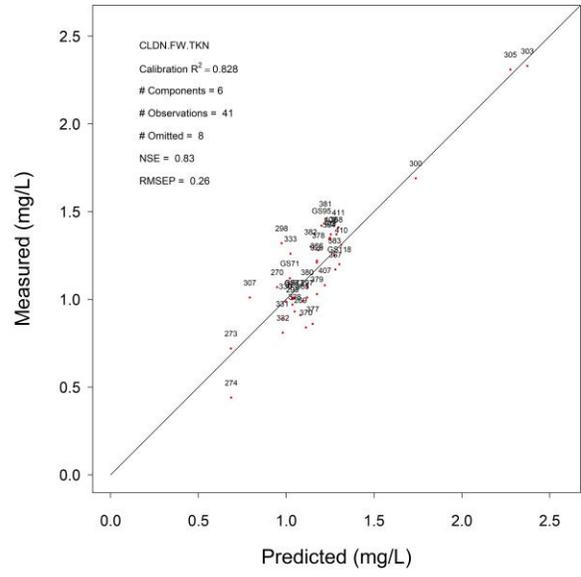
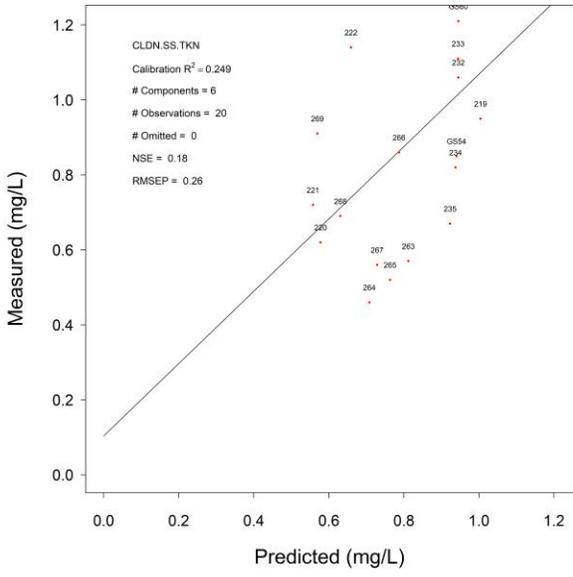


Figure A5. (continued).

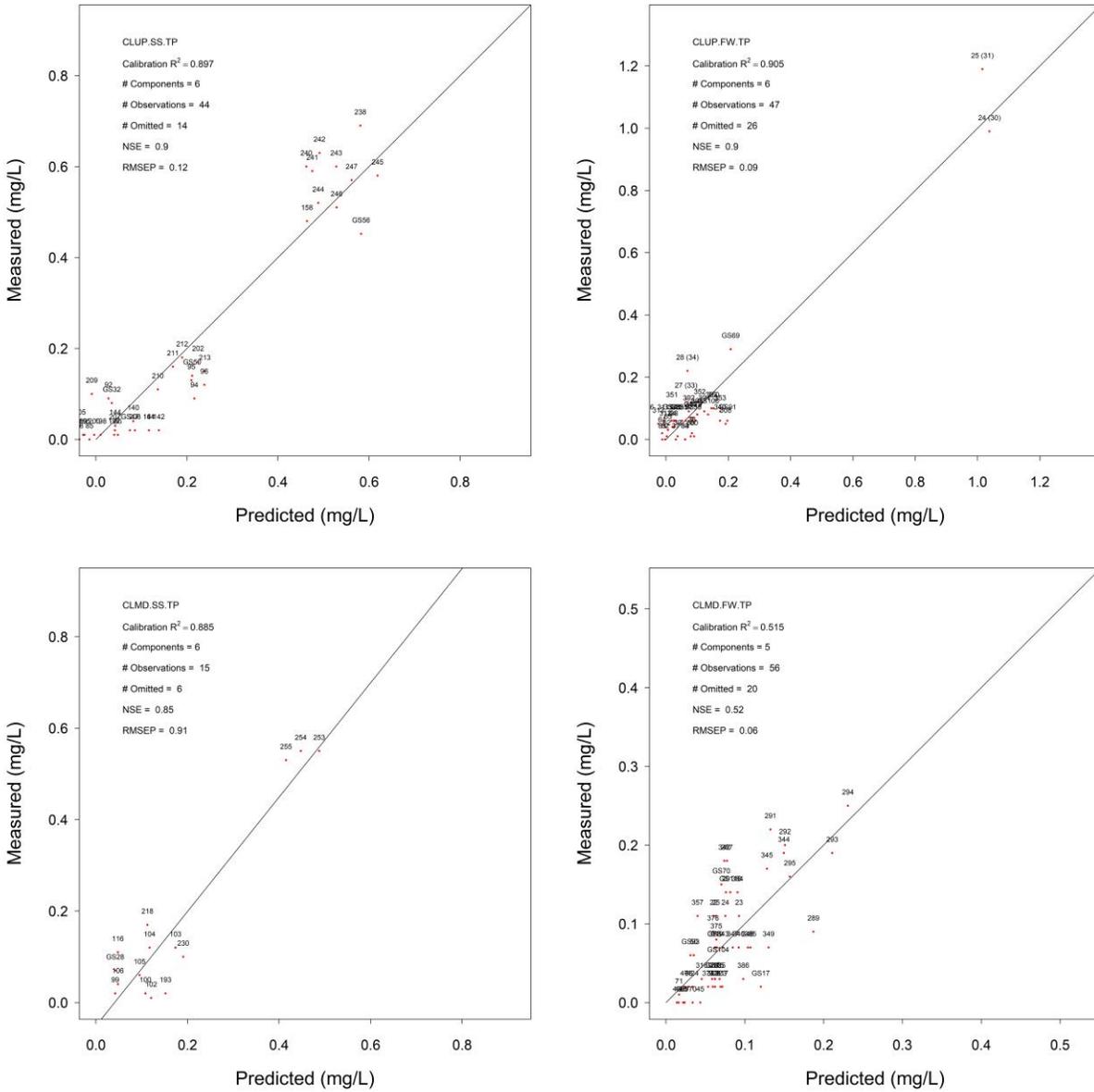


Figure A6. Regression relationships between measured total phosphorus concentrations from discrete sampling and predicted total phosphorus concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).

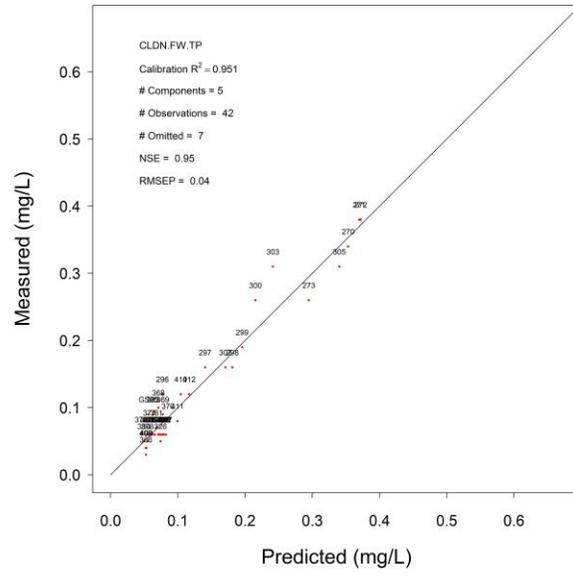
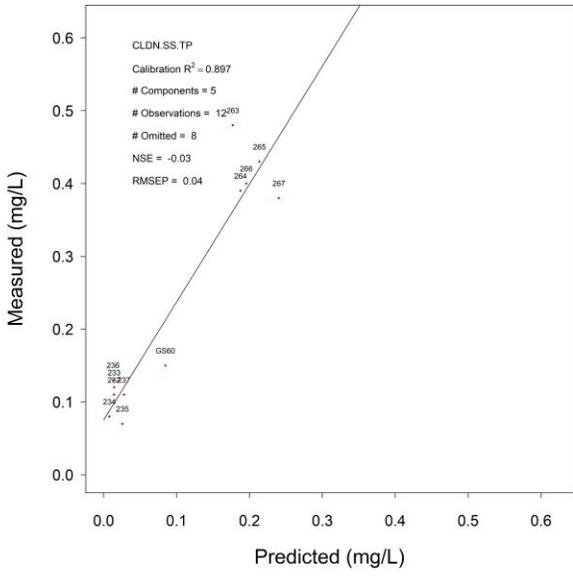


Figure A6. (continued).

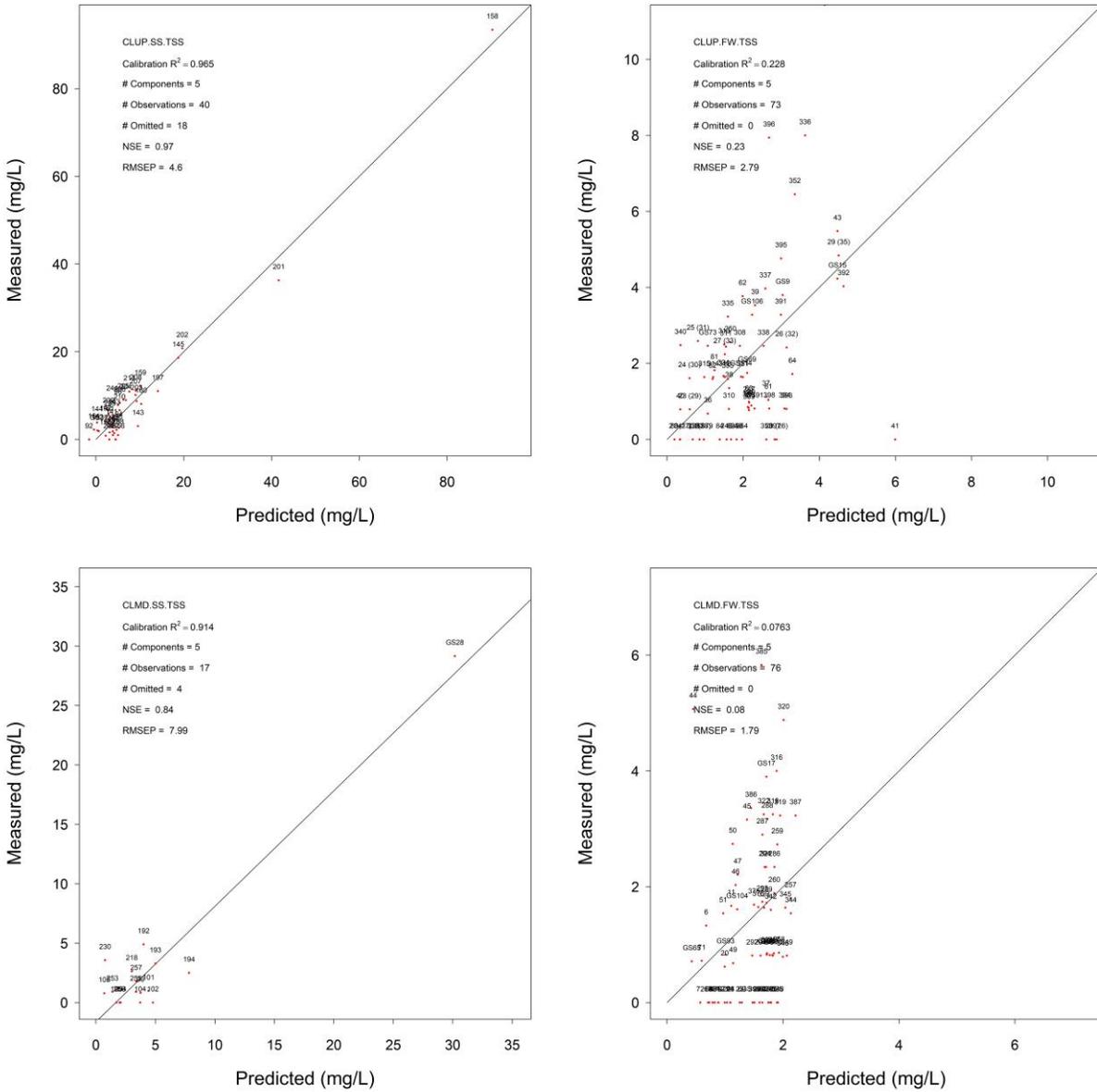


Figure A7. Regression relationships between measured total phosphorus concentrations from discrete sampling and predicted total phosphorus concentrations from PLSR calibrations; Spring/Summer (left column) and Fall/Winter (right column); CLUP, CLMD and CLDN (top to bottom).

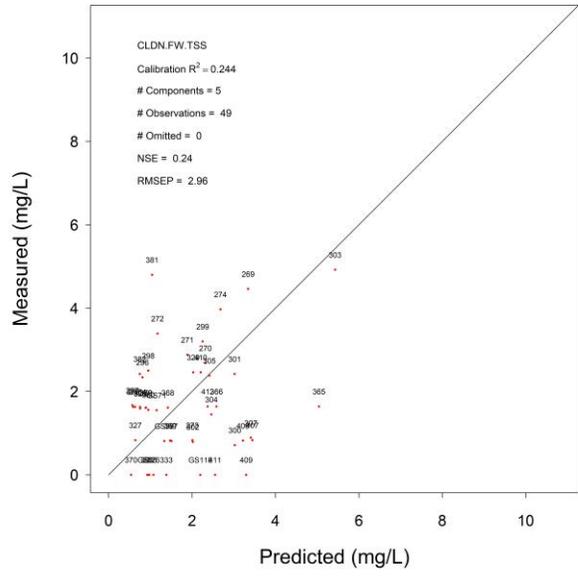
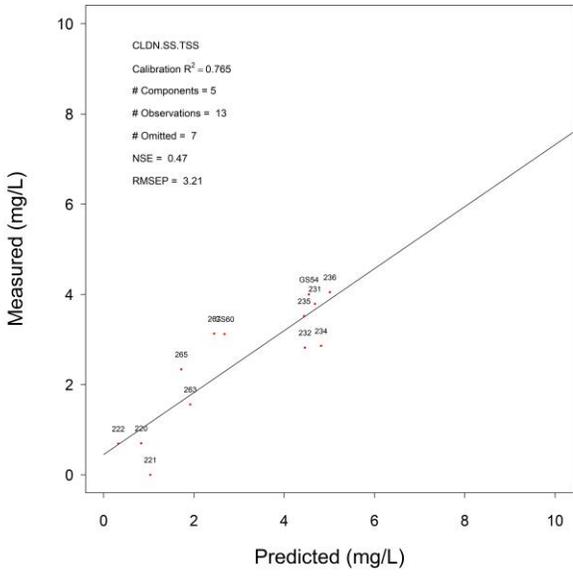


Figure A7. (continued).

Appendix B: DOC and Nitrate Time Series Chemographs and Hydrographs

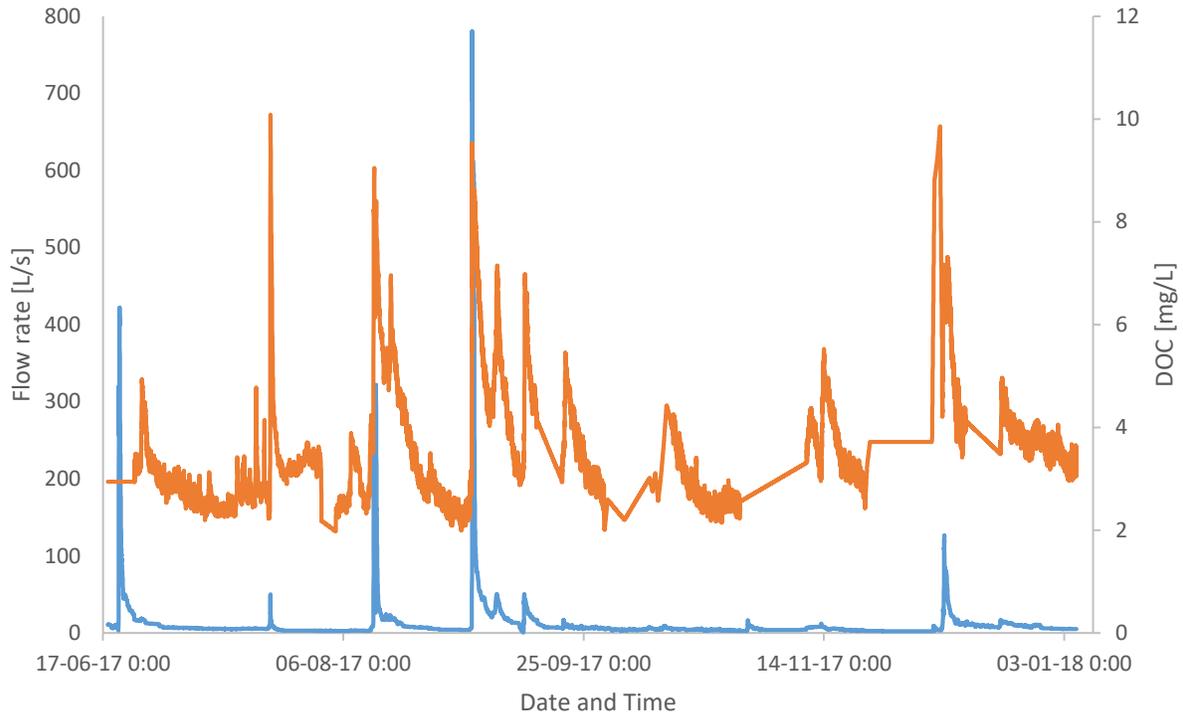


Figure B1. CLUP flowrate [L/s] (blue) and instantaneous DOC concentration [mg/L] (orange).

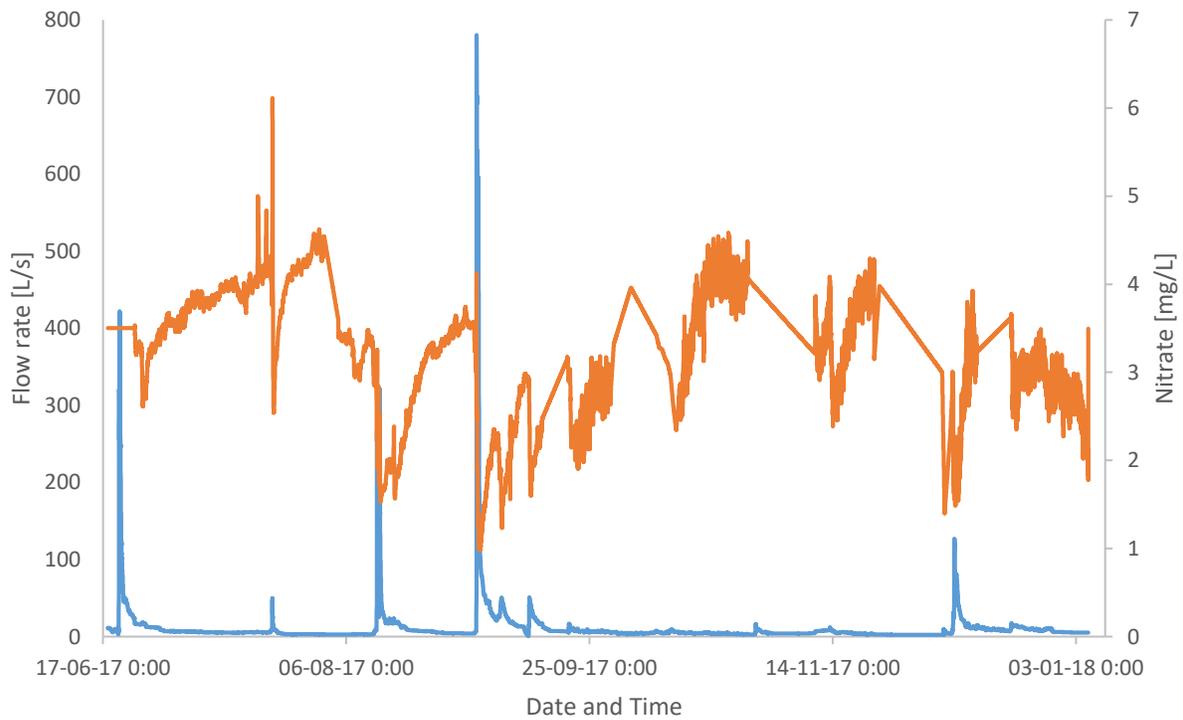


Figure B2. CLUP flowrate [L/s] (blue) and instantaneous nitrate concentration [mg/L] (orange).

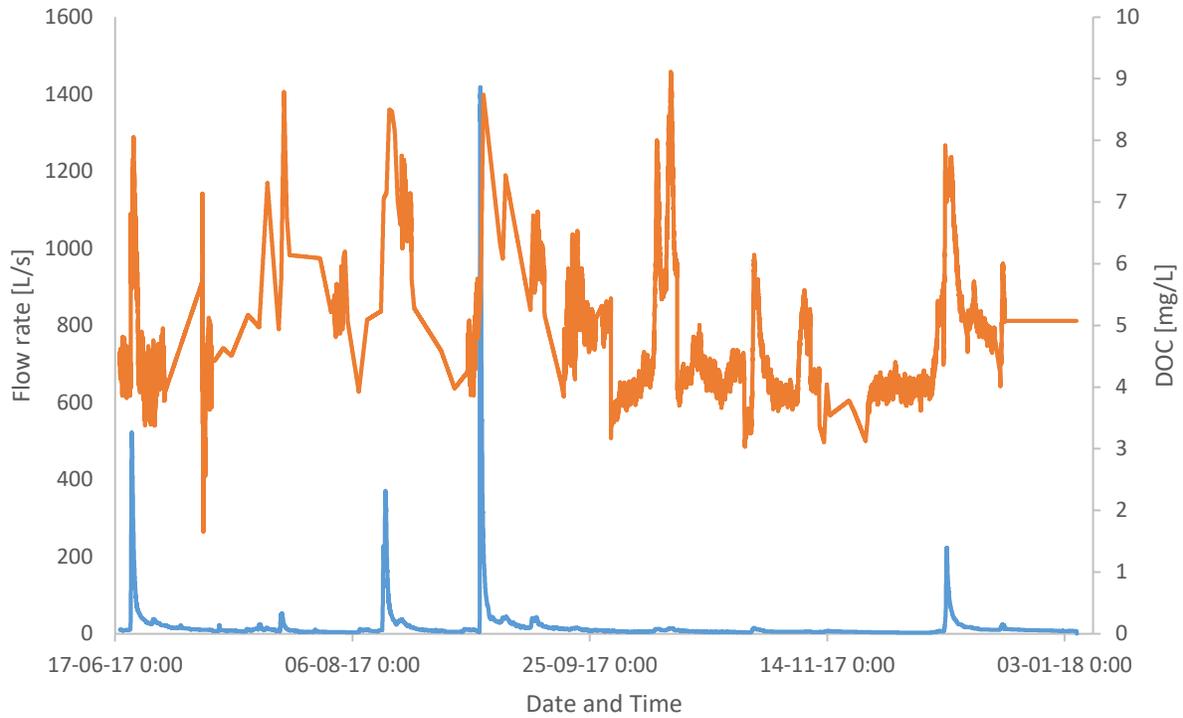


Figure B3. CLMD flowrate [L/s] (blue) and instantaneous DOC concentration [mg/L] (orange).

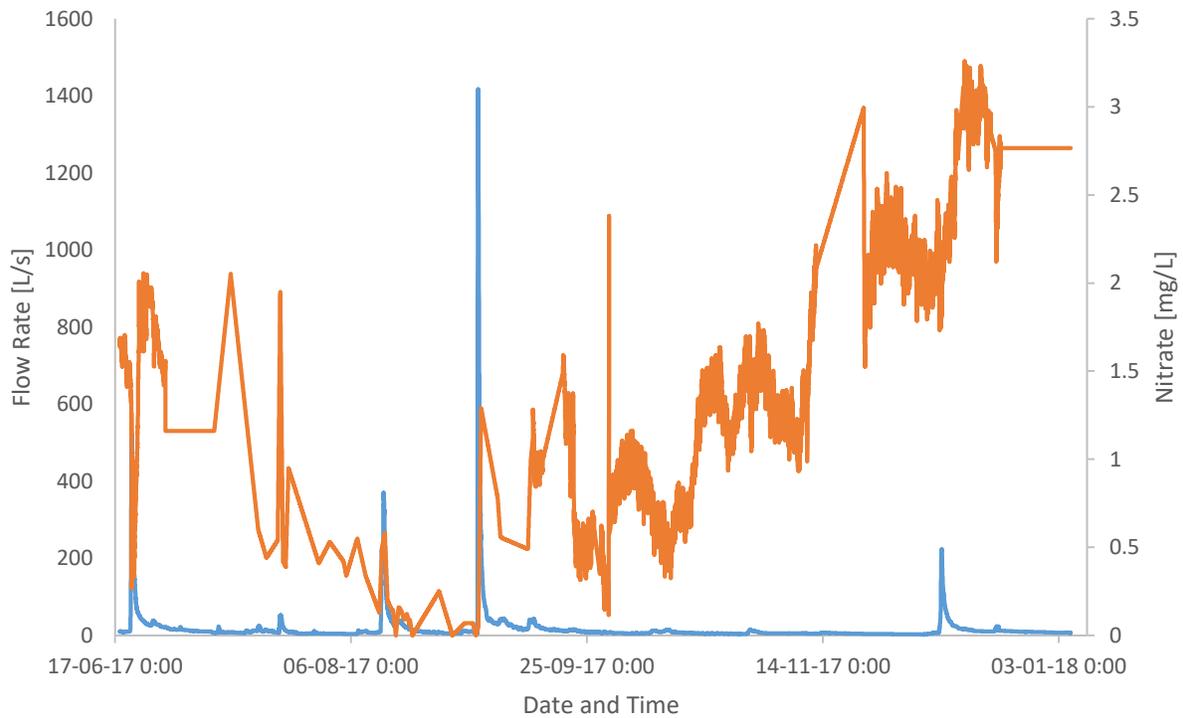


Figure B4. CLMD flowrate [L/s] (blue) and instantaneous nitrate concentration [mg/L] (orange).

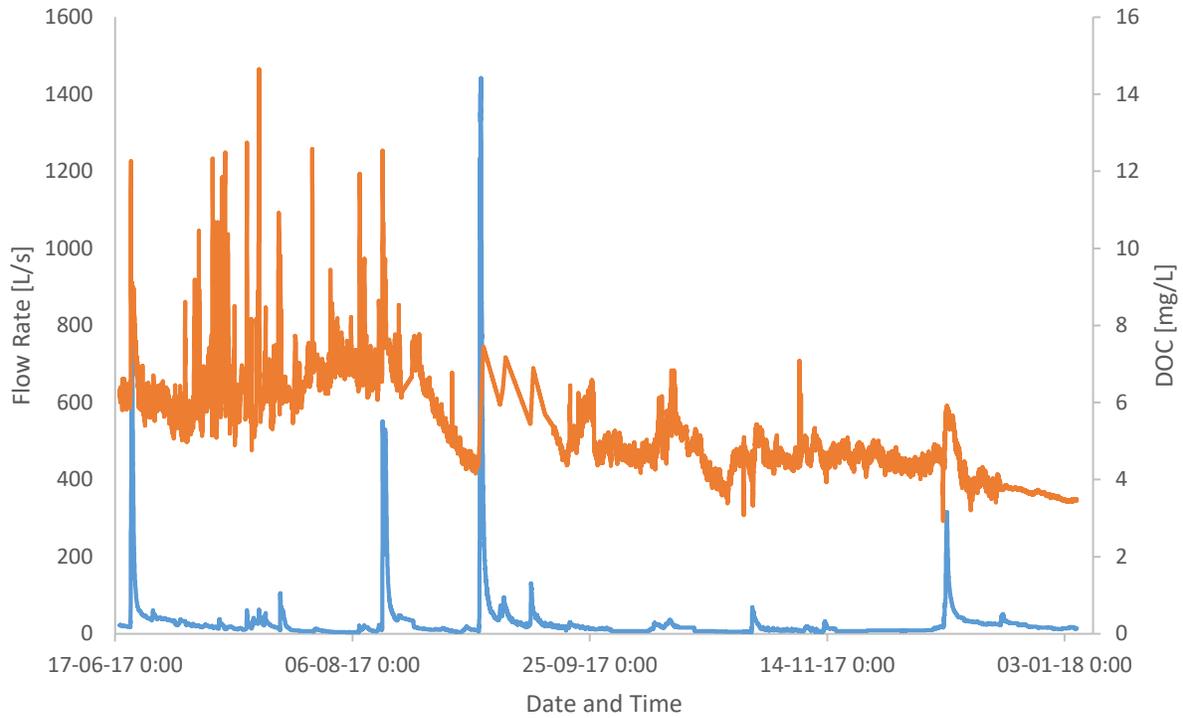


Figure B5. CLDN flowrate [L/s] (blue) and instantaneous DOC concentration [mg/L] (orange).

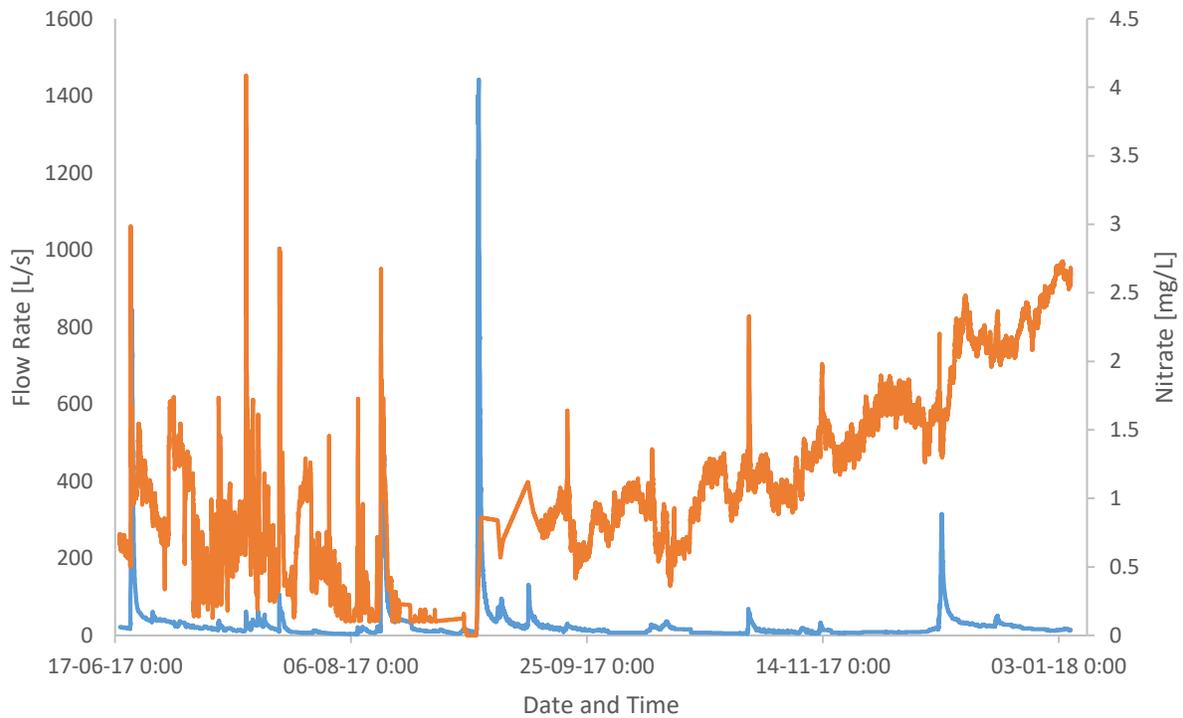


Figure B6. CLMD flowrate [L/s] (blue) and instantaneous nitrate concentration [mg/L] (orange).

Appendix C: Site Visit Checklists and Datasheets

SAMPLE COLLECTION DATE: ____/____/____ (dd/mm/yyyy)			
Site: Claridge Up (CLUP)			
S::CAN Checklist			
S::CAN S/N:			
S::CAN File Name			
Transfer S::CAN Data	Yes	No	
Data Visualization	Yes	No	
Previous Site Visit			
Before Cleaning:	File Name:		
DI water spectrum	Max:	Avg:	Min:
Air spectrum	Max:	Avg:	Min:
After Cleaning:	File Name:		
DI water spectrum	Max:	Avg:	Min:
Air spectrum	Max:	Avg:	Min:
Current Site Visit			
Before Cleaning:	File Name:		
DI water spectrum	Max:	Avg:	Min:
Air spectrum	Max:	Avg:	Min:
After Cleaning:	File Name:		
DI water spectrum	Max:	Avg:	Min:
Air spectrum	Max:	Avg:	Min:
Enter Logger Mode			
S::CAN Time difference	Fast	Slow	Difference:
S::CAN Start Time			
General Maintenance			
Marine Battery	Yes	No	Voltage:
Clean Manta Sensors	Yes	No	
Change pH solution	Yes	No	(Every 2 months)
Transfer Manta Data	Yes	No	
Manta Time Difference	Fast	Slow	Difference:
Calibrate Manta Time	Yes	No	
Start Manta Logging	Yes	No	
Clean ISCO Intake	Yes	No	
Clean Sontek and flume	Yes	No	
Download Sontek Data	Yes	No	
Start Sontek Logging	Yes	No	
Notes:			

Figure C1. Fillable data collection sheets used during each field visit to ensure consistent data collection.

SAMPLE COLLECTION DATE: ____/____/____ (dd/mm/yyyy)

Site: Claridge Up (CLUP)

ISCO Time			Checklist:		
Tablet Time			CD-B in sampler:	YES	NO
Time difference			CD-A in cooler:	YES	NO
			Time:		
			Program sampler: Delay to 12:00 AM		
			YES NO		
<i>Sample</i>	<i>Date/Time of Collection</i>	<i>Filter (E/B)</i> *	Battery Voltage		
CLUP-1			Amp-hr used since last disconnect		
CLUP-2			† If the Amp/hr used resets between visits you have lost power at some point. OR reset it on purpose to track power consumption		
CLUP-3			Flow measurement		
CLUP-4			Time		
CLUP-5				Flow velocity (m/s)	Depth (cm)
CLUP-6			ROB 4		
CLUP-7			ROB 3		
CLUP-8			ROB 2		
CLUP-9			ROB 1		
CLUP-10			ROC		
CLUP-11			Center		
CLUP-12			LOC		
CLUP-13			LOB 1		
CLUP-14			LOB 2		
CLUP-15			LOB 3		
CLUP-16			LOB 4		
CLUP-17			* Right/Left looking down stream		
CLUP-18			Notes:		
CLUP-19					
CLUP-20					
CLUP-21					
CLUP-22					
CLUP-23					
CLUP-24					
CLUP-A					
CLUP-B					

*Event (E) or Baseflow (B)

Figure C1. (continued).

Appendix D: Data Processing Flow Chart

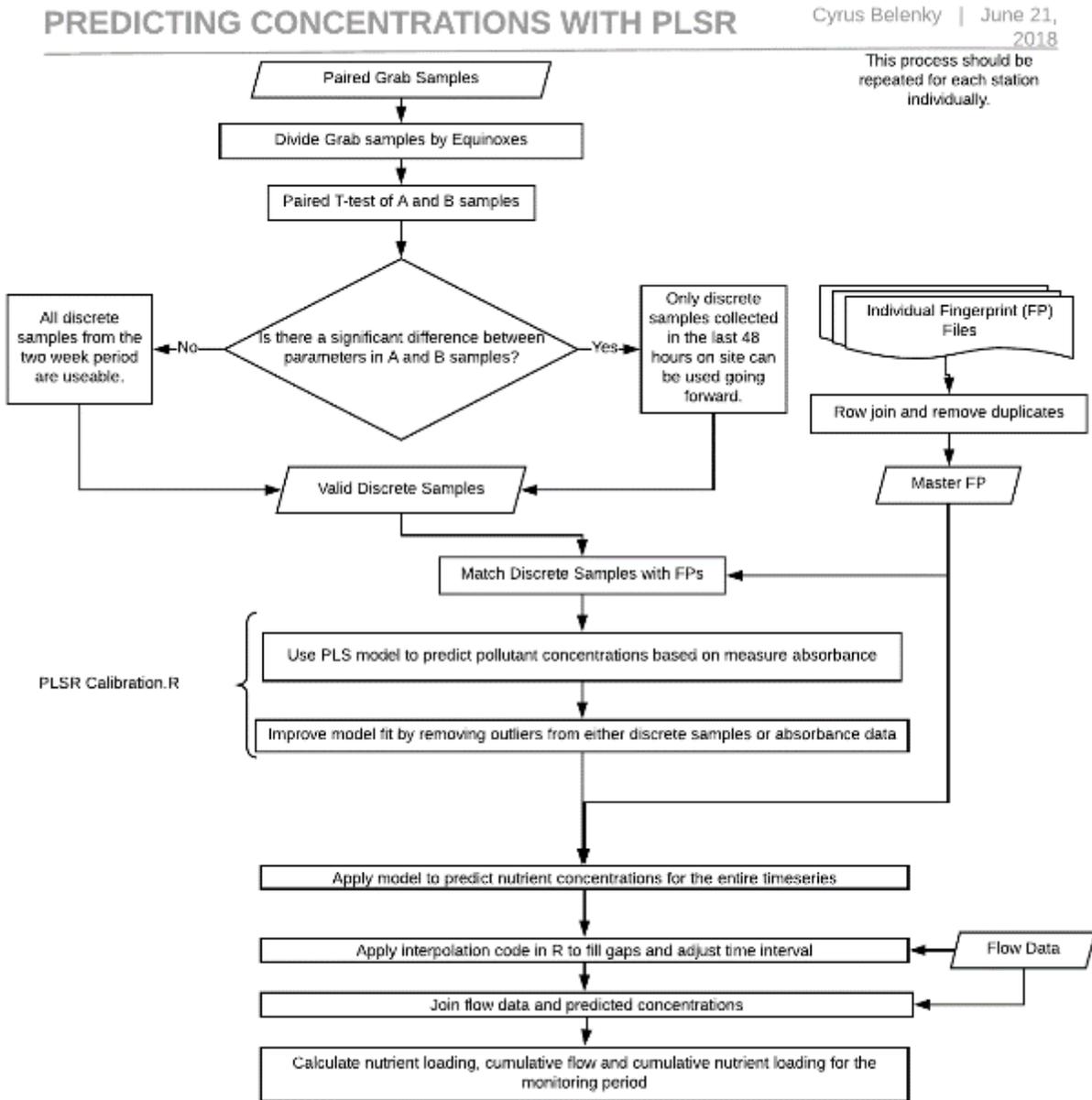


Figure D1. Data Processing and PLSR flowchart created to visualize the method.

Appendix E: Double Mass Curves Including Little River Influences

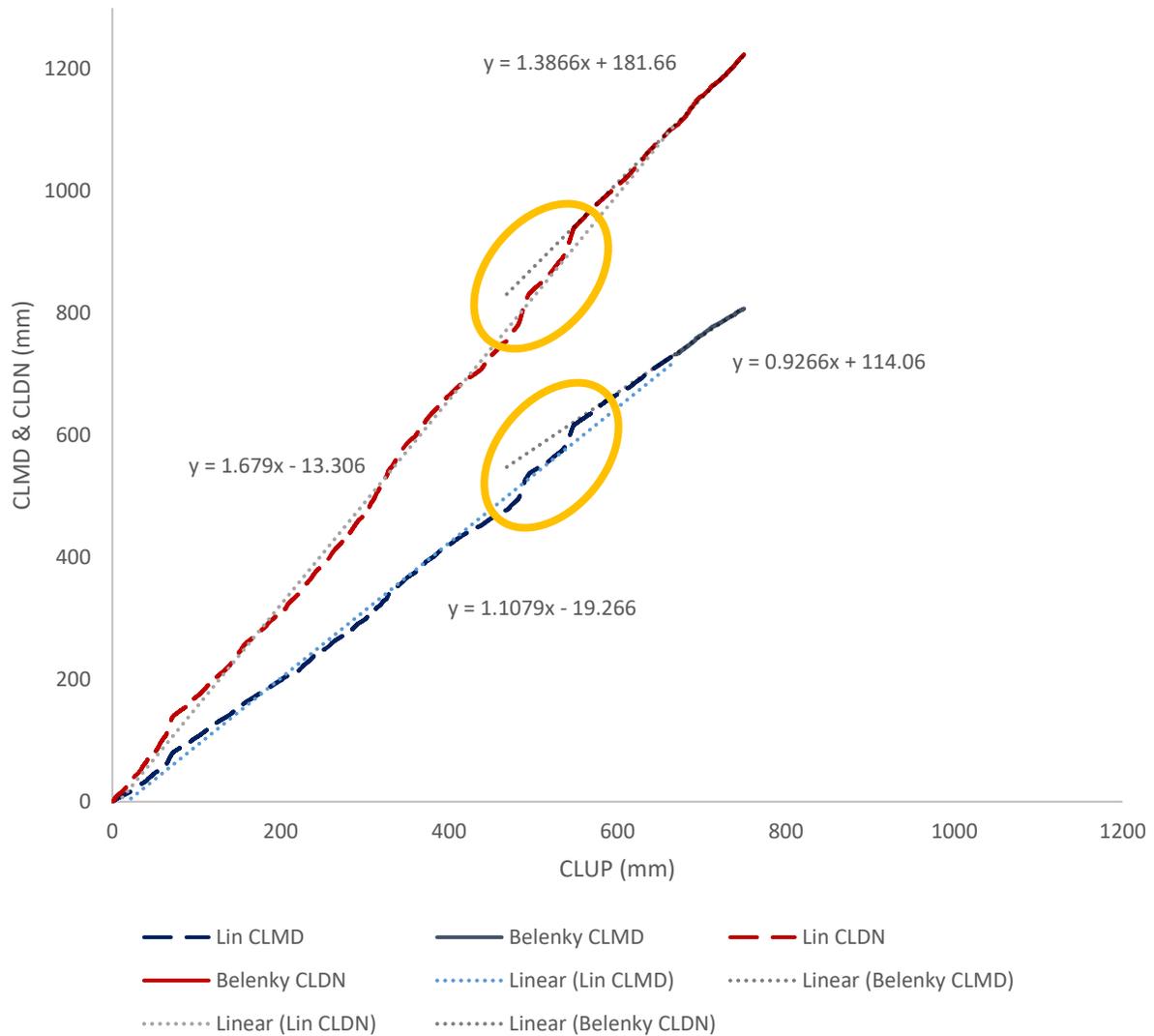


Figure E 1. Cumulative volume CLMD (solid) & CLDN (dashed) (mm) vs. cumulative volume CLUP (mm) and one-to-one line (long dashed). Events where the Little River influenced water quality in The Canal are circled in orange.

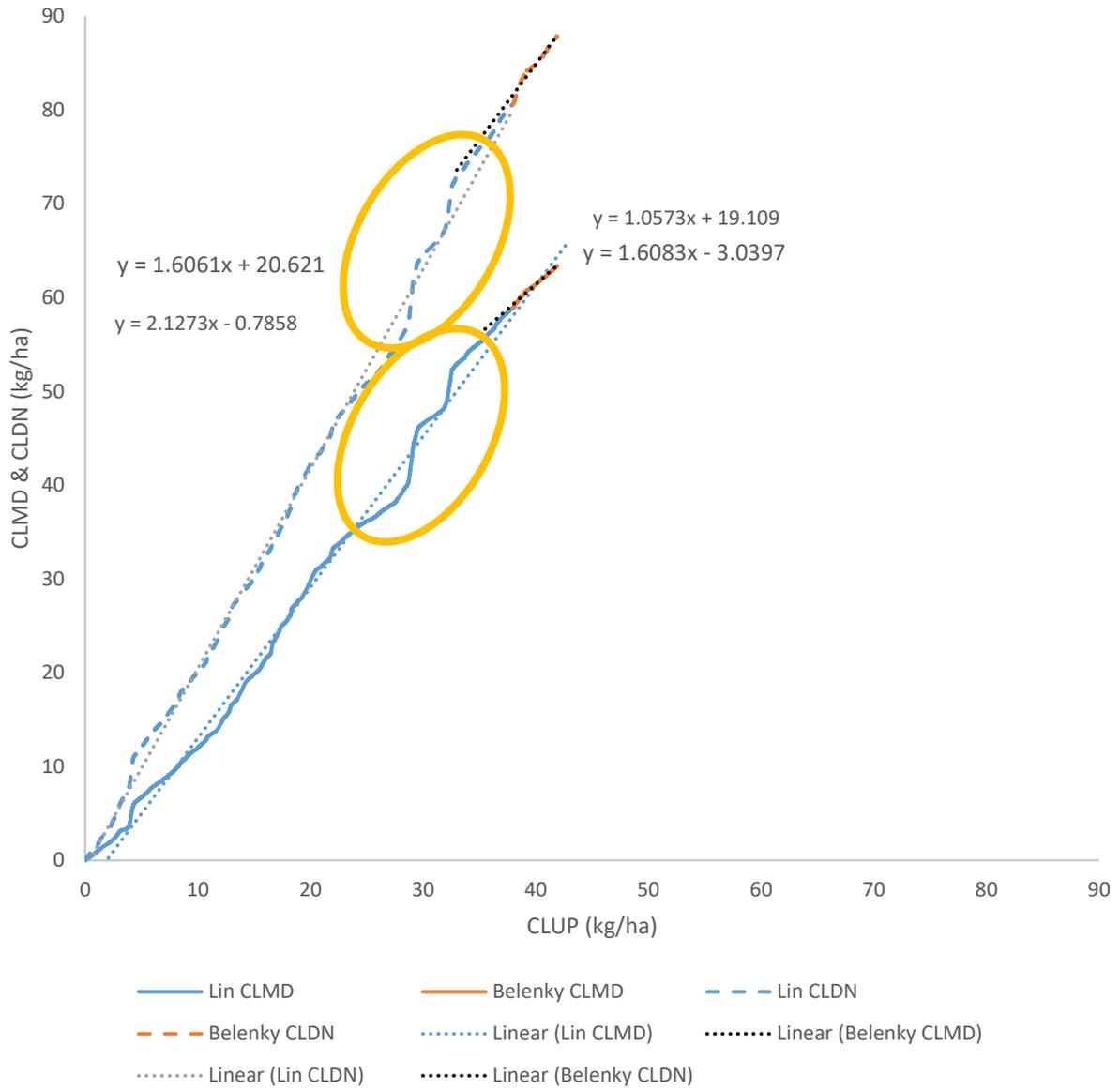


Figure E 2. Cumulative DOC CLMD (solid) & CLDN (dashed) (kg/ha) vs. cumulative DOC CLUP (kg/ha) and one-to-one line (long dashed). Events where the Little River influenced water quality in The Canal are circled in orange.

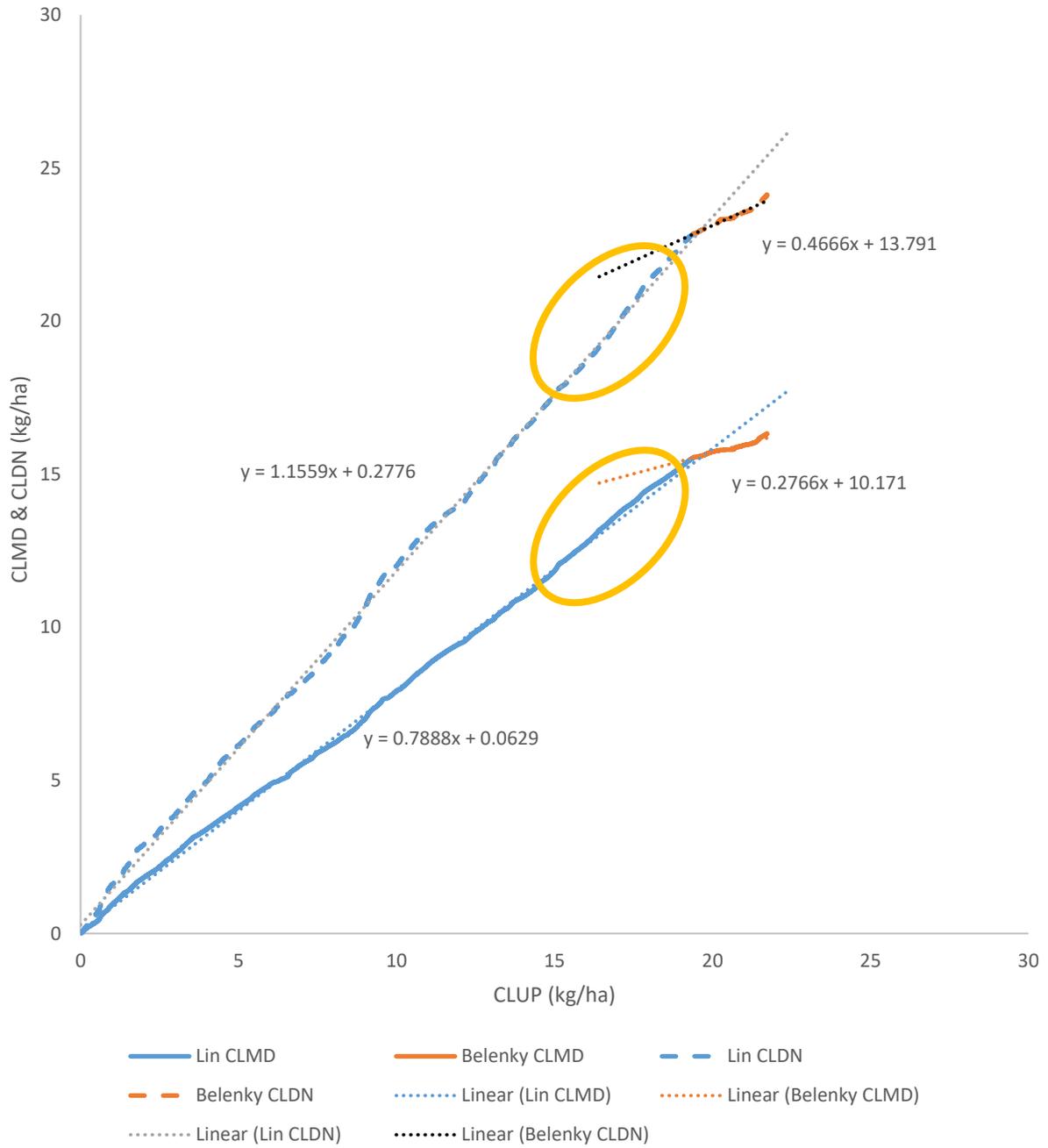


Figure E 3. Cumulative nitrate CLMD (solid) & CLDN (dashed) (kg/ha) vs. cumulative nitrate CLUP (kg/ha) and one-to-one line (long dashed). Events where the Little River influenced water quality in The Canal are circled in orange.