ABSTRACT

USRY, BRIAN P. Nitrogen loading in the Neuse River Basin, North Carolina: The RiverNet monitoring program. (Under the direction of William J. Showers.)

Coastal eutrophication is a major concern in many estuarine systems around the world. Nitrogen has been demonstrated to be the limiting nutrient in many coastal systems. In recent years, the Neuse River Basin in North Carolina has experienced large fish kills, which has heightened the need for better monitoring of riverine nitrogen loading. The RiverNet Monitoring Program was initiated to provide high-resolution (hourly) measurement of nitrate (NO_3^-) using in-stream nutrient analyzers. Three sites on the Neuse River mainstem and two on Contentnea Creek were monitored continuously from January 2001 through December 2002. Bear Creek, an agricultural watershed, was continuously monitored from May 2002 to May 2003. Water samples were taken for analysis of nitrogen speciation: dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON) and total dissolved nitrogen (TDN). Large NO_3^- variability was discovered at sites downstream of wastewater input and urban runoff, while the variability diminished farther downstream. The NO_3^- load in the Neuse River mainstem at Fort Barnwell was $11 \pm 1.0 \times 10^5$ kg N yr^{-1}, with 26% ($2.9 \pm 0.5 \times 10^5$ kg N yr^{-1}) of that total coming from Contentnea Creek during the 2001-02 study period.

Nitrate yields in the Neuse River mainstem and Contentnea Creek Basin varied from 99 to 130 kg N km^{-2}, while Bear Creek exceeded 810 kg N km^{-2}. δ^{15}N and δ^{18}O isotopes of NO_3^- provide a way to characterize monitoring sites as urban, agricultural, or mixed source N-dominated.

NITROGEN LOADING IN THE NEUSE RIVER BASIN, NORTH CAROLINA:

THE RIVERNET MONITORING PROGRAM

by
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DEDICATION

This effort is dedicated to my parents, whose love, support, and patience have helped sustain me throughout this process.

BIOGRAPHY

Growing up in the Appalachian foothills of Alabama, Brian Usry became interested in water quality at a very early age. Living near Weiss Lake, proclaimed the “Crappie Capital of the World” and his parents’ decision to raise catfish on the family farm impacted his decision to pursue a career in hydrology. While attending college, he spent two summers at the Marine Environmental Sciences Consortium on Dauphin Island, Alabama where he became interested in marine processes. In 1997, he earned a bachelor’s degree in geology from the University of South Alabama. Upon graduation, Brian returned home to work in construction building in-ground swimming pools. In 2000, he decided to return to school and pursue a master’s degree in marine science at North Carolina State University. Working with the RiverNet Monitoring Program has allowed him to focus his research on nitrogen processes in freshwater ecosystems. Brian plans to pursue secondary science education in Alabama after graduation.

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Chapter 1 Introduction

Nutrient loading to surface waters has increased dramatically in recent decades due to anthropogenic alteration of biogeochemical cycles (Galloway et al., 1995; Howarth et al., 1996; Vitousek, 1997; Caraco & Cole, 1999). Howarth et al. (1996) estimate that total nitrogen (TN) delivered to the North Atlantic from temperate regions has increased 5 to 20 fold over natural pre-industrial conditions. Human population growth and the associated activities of increased food production (agriculture and livestock), energy consumption, and waste disposal have facilitated this trend (Heaton, 1986; Vitousek et al., 1997). Diminished water quality can result from excessive nitrogen loading causing public health concerns and stress to aquatic ecosystems.

Contamination of drinking water by nitrate (NO_3^-) has been linked to methemoglobinemia or “blue baby syndrome”, a potentially fatal condition in infants (Metzler & Stoltenberg, 1950; Fan & Steinberg, 1996). There is also strong evidence to support a linkage between many forms of cancer such as non-Hodgkin’s lymphoma and elevated nitrate concentrations (Weisenburger, 1990; Ward et al., 1996). Because of these risks, the World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) have established a maximum drinking water concentration of 10mg/L for NO_3^-N (U.S. EPA, 1994; WHO, 2004).

Nitrogen is an essential nutrient for primary production and a limiting factor for many aquatic ecosystems (Nixon, 1995; Howarth et al., 1996; Paerl, 1997; Vitousek et al., 1997). However, many watersheds now export more nitrogen than is taken up by the ecosystem. In the Mississippi River Basin, nitrate concentrations have doubled since 1965 and nitrate levels in major rivers in the northeastern U.S. have tripled since the early 1900's (Turner &

Rabalais, 1991; Justic et al., 1995; Howarth et al., 1996; Vitousek et al., 1997; Alexander et al., 2000; Goolsby & Battaglin, 2001). This excess nitrogen can cause overproduction of phytoplankton blooms, which in turn can lead to hypoxic or anoxic conditions in estuarine and coastal waters (Vitousek et al., 1997; Paerl, 1997; Pinckney et al., 1998). Coastal eutrophication is a growing problem in many estuarine areas around the world. Over 40% of the estuaries in the U.S. suffer from eutrophication with the Atlantic coast the most severely affected (Bricker et al., 1999).

The effects of excessive nitrogen loading are more pronounced in estuarine ecosystems, and consequently much research has focused on these areas. Since most of this dissolved inorganic nitrogen (DIN) and organic nitrogen (DON) originates upstream, regulations aimed at alleviating the eutrophication effects in estuaries must be enacted in upstream watersheds. Rivers carry a major portion of the nitrogen load to the world's oceans (Howarth et al., 1996). Large rivers carry tremendous amounts of DIN and DON, and are variable on seasonal scales (Meybeck, 1982; Tonderski et al., 1995; Stalnacke et al., 1999a; Goolsby et al., 2001; Hooper et al., 2001). Long duration hydrographs and seasonally predictable discharge allow these larger rivers to be characterized through infrequent (monthly) water sampling and application of coefficients based on land-use categories (Beaulac & Reckow, 1982; Tonderski et al., 1995; Stalnacke et al., 1999a;b; Battaglin et al., 2001; Goolsby et al., 2001; Hooper et al., 2001). The smaller constituent watersheds that discharge into these larger river basins are more prone to rapid temporal variations induced by changing hydrological conditions and influences from multiple pollution sources (Littlewood, 1995; Goolsby et al., 2001). Using the same sampling methods in both cases can result in diminished resolution of nitrogen loading (Reinelt & Grimvall, 1992). Most high-resolution nitrogen delivery studies have been limited to watersheds dominated by one nitrogen input source, such as agriculture or wastewater (Thomas et al., 1992; Merot et al., 1995; Caissie et al., 1996; Jordan et al., 1997) or multiple sources measured at one location within a larger watershed (Soerens & Nelson, 2002). Watersheds that have larger percentages of agricultural lands tend to discharge proportionally greater amounts of N (Mason et al., 1990; Jordan et al., 1997; Bohlke, 2002). Smaller watersheds may show no correlation of loading with land-use, while larger basins may incorporate other anthropogenic nutrient sources such as atmospheric deposition, wastewater discharge, or animal operations (Thomas et al., 1992; Jordan & Weller, 1996; Jordan et al., 1997; Whitall et al., 2003).

The Neuse River Basin in North Carolina has received considerable attention in recent years due to chronic eutrophication and extensive late-summer fish kills (Burkholder et al., 1992; 1995; 1999; Paerl et al., 1995; Paerl, 1997; Pietrafesa & Miller, 1997; Pelley, 1998; Pinckney et al., 1998; Burkholder et al., 1999; NCDWQ, 2001; NCDWQ, 2002). Since the North Carolina Division of Water Quality began keeping records of fish kills in 1996, there has been a general increasing trend with the Neuse having the highest number of recorded events (NCDWQ, 2001; NCDWQ, 2002). Previous attempts to characterize the extent of nitrogen loading in the Neuse River Basin have used equations derived from low-resolution sampling and/or land-use coefficients for estimation of diffuse nitrogen loading (Dodd et al., 1992; Stow et al., 2001; Borsuk et al., 2002). Land use export coefficients are dependent on a correlation between land use and nutrient load (Beaulac & Reckhow, 1982; Dodd et al., 1992). These may be poor predictors because export rates can vary for a given land use category depending upon hydrogeology and climate (Frink, 1991). Nitrate isotopes, ^{15}N and ^{18}O; have been used by a number of authors to characterize N inputs as well as in-stream changes associated with N loss (Showers et al., 1990; Kendall, 1998; Sebilo et al., 2003)

The objectives of this study were to: 1) use in-stream monitoring data to calculate the nitrate load at locations in the Neuse River, Contentnea Creek, and Bear Creek; 2) establish some of the controlling factors on nitrate loading and nitrogen speciation; and 3) contrast N inputs between point and non-point source-dominated sites using stable isotopes ^{15}N and ^{18}O.

Chapter 2 Background

2.1 Study Area

The Neuse River basin is located in the east-central portion of North Carolina (Figure 1). Beginning at the confluence of the Flat and Eno Rivers, it flows 300 kilometers eastward through the cities of Durham, Raleigh, Clayton, Smithfield, Goldsboro, and Kinston before entering the estuary near New Bern, NC. The Neuse River basin contains 5,600 freshwater stream kilometers and has a drainage area of 16,149 km^2 making it the third largest drainage basin in the state (NCDENR, 1993). Fourteen subbasins divide the watershed (NCDENR, 1993). The RiverNet monitoring program covers 10,132 km^2 (63%) of the basin's area from Falls Lake (FL) to Fort Barnwell (NRB). Included are the tributaries Contentnea Creek, Bear Creek, Middle Creek, Swift Creek, Black Creek, and Little River (Figure 2). Land use varies among the watersheds in the monitoring area (Figures 3 & 4). A total of 22 sites were sampled monthly, six continuously monitored, from January of 2001 to January of 2003 (Table 1).

The Neuse Basin has two physiographic regions: the Piedmont and the Coastal Plain. The Piedmont extends from just west of the Neuse basin to below Smithfield, where the Coastal Plain begins south and east of the "Fall Line". Triassic basement rocks underlie the headwaters of the Neuse River, while a fractured complex of Paleozoic igneous and metamorphic rocks overlain by an unconsolidated soil regolith forms the geology of the remainder of the Piedmont (McMahon & Lloyd, 1995; Daniel & Dahlen, 2002). The Coastal Plain is composed of a series of eastward dipping sand and limestone aquifers separated by clay confining units underlain by the crystalline bedrock of the Piedmont (Winner & Coble, 1989, 1996; Giese et al., 1992). There are nine distinct formations from west to east: a

Quaternary unconsolidated surficial layer, Yorktown, Pungo River, Castle Hayne, Beaufort, Peedee, Black Creek, and the Upper and Lower Cape Fear Formations (Winner & Coble, 1989; Giese et al. 1992).

Rainfall does not vary greatly across the Neuse Basin (NCSCO, 2003; Whitall et al., 2003). Annual rainfall in the Neuse Basin varies from 910 mm in the Piedmont to around 1270 mm near the coast (Wilder et al., 1978; Giese et al., 1992; McMahon & Lloyd, 1995). Discharge patterns were different between the two years, as a relatively wet early summer and dry fall/winter characterized 2001, while 2002 was extremely dry during the summer and wet in the autumn and winter months (Figure 5). July 2001 to June 2002 was the driest 12-month span on record with rainfall amounts more than 300mm below the annual mean (NCSCO, 2003; NOAA, 2004).

Falls Lake, a multi-use reservoir constructed in 1983, impounds the upper 35 km of the basin and regulates flow in the mainstem (NCDENR, 1993). The dam impounds an average volume of 1.90 x 10^8 m^3 of water (Hitt, 1990). Minimum flow release is 3 m^3/s (100 ft^3/s) during the summer months and 2 m^3/s (65 ft^3/s) during the winter months (Weaver, 1998). Heath (1994) mapped major groundwater discharge areas in the North Carolina Coastal Plain where groundwater contributes to the surface water flow. Groundwater discharge in the Neuse River Basin is predominately from shallow surficial aquifers (Giese et al., 1992; Spruill et al., 1998; Weaver, 1998; Daniel & Dahlen, 2002). Many smaller streams derive more than 50% of their total flow from groundwater during low-flow conditions (Weaver, 1998).

2.2 Nitrogen in watersheds

Nitrogen is the major component of the atmosphere (78%) and an essential element for life, forming one of the most complex biogeochemical cycles on Earth (Heaton, 1986; Berner and Berner, 1987). The processes that control nitrogen speciation include: biological nitrogen fixation, denitrification, nitrification, volatilization, mineralization, and uptake and assimilation (Stoddard, 1994; Kendall, 1998). In water, nitrogen can occur as an anionic species, nitrate (NO_3^-) or nitrite (NO_2^-), a cationic species, ammonium (NH_4^+), as dissolved molecular N_2 (gas), or as part of an organic solute (Hem, 1992). Nitrate is very soluble and relatively stable, and can therefore be transported long distances in aquatic ecosystems. Nitrite is microbially converted to nitrate in oxygenated waters. Dissolved organic nitrogen (DON) forms the largest fraction of total dissolved nitrogen (TDN) in many watersheds. However, the amount of DON that is biologically available is not well understood and depends on the size of the organic molecule and input source (Seitzinger et al., 2002b). Ammonium is easily sorbed onto particles or preferentially taken up relative to nitrate by bacteria or algae and is generally found in lower concentrations than nitrate or dissolved organic nitrogen (Stanley, 1983; Hem, 1992; Stoddard, 1994). Due to its stability in oxygenated waters, nitrate is commonly the dominant inorganic form found in riverine environments (Meybeck, 1982; Puckett, 1994; Clark et al., 2000; Battaglin et al., 2001; Hooper et al., 2001). Pearl (1987) estimated that 90% of the inorganic nitrogen delivered to the Neuse estuary is in the form of nitrate.

Denitrification is an important microbial process in aquatic environments, in which NO_3^- is biologically reduced to a gaseous form of nitrogen (N_2, NO, or N_2O) (Stoddard, 1994; Kendall, 1998). The result is a net loss of biologically available nitrogen with the conversion to inert N_2 gases. Many studies reported in-stream losses of up to one-third of the nitrogen inputs (Seitzinger, 1988; Jordan &Weller, 1996; Howarth et al., 1996; Jordan et al., 1997) and some have implied losses of over 75% (Seitzinger et al., 2002a). Alexander et al. (2000) demonstrated that in-stream losses are related to depth with little occurrence in deeper channels. A large portion of nitrogen may also be lost in the landscape before it reaches a drainage pathway (van Breeman et al., 2002). Bacterial denitrification in groundwater is driven by the presence of elevated organic carbon levels, which can result in lower nitrate concentrations (Korom, 1992; and Spruill et al., 1996). Groundwater and surface water interactions, whether through lateral movement through riparian and wetland areas or vertical movement through hyporheic bottom sediments, can affect stream chemistry by enhancing denitrification (Seitzinger, 1988; McMahon & Bohlke, 1996; Hinkle et al., 2001; Seitzinger et al., 2002a). However, groundwater may also flow underneath riparian areas and discharge to streams unaffected by denitrification (Bohlke and Denver, 1995; Burt et al., 1999) or be subject to longer flow paths with water discharged that is not indicative of recent nutrient activity in the watershed (Puckett et al., 2002). Tile drains in agricultural areas can also enhance movement of groundwater to streams (Jacobs & Gilliam, 1983). Biological assimilation is another process by which nitrate can be removed. Assimilation or uptake by primary producers tends to be more pronounced in heavily forested watersheds where the level of biomass is high (van Breeman et al., 2002).

2.3 Nitrogen Sources

2.3a Point source N input

Maybeck (1982) estimates that, approximately one third of the TDN (both organic and inorganic) in the world's river water is from anthropogenic pollution. According to the 2000 U.S. Census, approximately 1.4 million people live in the Neuse River Basin, mostly congregated in municipal areas in the upper basin (Durham and Raleigh). In the Neuse River Basin, inputs up to 90% of TDN are found during low flow conditions in waters downstream from major urban areas (i.e. Raleigh, Harned, 1980). Nitrogen discharges to surface water via well-defined discharge points (i.e. pipe or ditch) are called point sources. Point source inputs include treated wastewater, industrial effluent, and storm water discharge (NCDENR, 2002). In watersheds with high population densities, point source sewage discharge may explain increased nitrate loading in receiving streams (Cole et al., 1993). Wastewater treatment plants (WWTPs) dominate this point source discharge, the largest of which are located in the highly populated upper basin. In the Neuse Basin, point dischargers must operate under National Pollutant Discharge Elimination System (NPDES) permits (U.S. EPA, 1972, 1977, 1987; NCDENR, 2002). There are 157 permitted wastewater dischargers, which are allowed to release 8.63×10^5 m^3 of treated effluent per day into the Neuse and its tributaries (NCDENR, 2002, Figure 6). Twenty-seven are considered "major", discharging more than 3800 m^3 day^{-1} each and accounting for 8.33×10^5 m^3 day^{-1} (96%) of the total maximum permitted point source effluent to the basin (NCDENR, 2002). In addition, there are 147 permitted storm water dischargers (NCDENR, 2002).

2.3b Non-point source N input

Diffusion of nitrogen from indiscriminate areas is called non-point discharge (Kendall, 1998). Non-point sources include leaching of fertilizers and land-applied wastes from agricultural areas, atmospheric deposition from urban centers and concentrated animal feeding operations (CAFO's), and runoff (Dodd et al., 1992; Paerl et al., 1995; Gilliam et al., 1996; Paerl, 1997; Aneja et al., 2001; Karr et al., 2001; NCDENR, 2002). If more N is applied to cropland than can be utilized by the plants, the excess N has the potential to be leached into groundwater or carried via runoff to streams. Nitrogenous fertilizer usage in the Neuse River Basin increased by 400% from the mid-1940's to the 1980's (Jacobs & Gilliam, 1985; Stanley, 1988). Best management practices (BMP) in agriculture have led to improved nitrogen application in the basin, thus reducing the amount of fertilizer needed to sustain crop yields (Stow et al., 2001; Wossink & Osmond, 2002; Osmond, 2003). Agriculture has been traditionally linked to increased reactive nitrogen in aquatic systems (Bohlke & Denver, 1995) and is believed to contribute approximately 60% of the N load in the Neuse River Basin (NCDENR, 1993; 1998).

In 2002, it is estimated that 9.6 million swine were raised annually in North Carolina (NCDA, 2002). In addition, 45 million turkeys and 735 million broilers (chickens) are grown annually in the state (NCDA, 2002). In the United States, North Carolina ranks number two in swine production behind Iowa, number one in turkey production, and near the top in broiler production. Most of these animals are consolidated into large farms with more than 2,000 head due to economic favorability (Figure 7). Waste lagoons located at these concentrated animal feeding operations (CAFO's) have been shown to release large amounts of ammonia to the atmosphere through volatilization (NCDENR, 1999; Walker et al., 2000;

Aneja et al., 2001). Land applied wastes can also release ammonia and/or contribute to nitrate in groundwater and receiving streams (Stone et al., 1998; Mallin, 2000; Karr et al., 2001).

Atmospheric contribution to the non-point nitrogen load is believed to be substantial, however, estimates range widely and are subject to local variations (Howarth et al., 1996; Walker et al., 2000; Whitehall et al., 2003). Nitrogen emissions derived from automobiles and point sources occur as NO_x (N-oxides), while emissions from animal operations occur as NH_x (NH_3 + NH_4^+) (Aneja et al., 1998, Walker et al., 2000; Karr et al., 2001). In North Carolina, the largest sources of this nitrogen are automobiles (23.7%), point sources (23.6%), and swine (20.6%) (Aneja et al., 1998, 2001). These emissions eventually make their way to surface water through dry deposition and rainfall, whether direct or indirect (runoff). Whitall et al. (2003) estimates that up to 50% of the total "new" nitrogen supplied to the Neuse estuary is from wet atmospheric deposition based on N retention models. Dry atmospheric deposition amounts are comparable in magnitude to wet deposition in some instances (Likens et al., 1974; Fisher & Oppenheimer, 1991).

2.3c Nitrate isotopes

Isotopes of nitrogen and oxygen are measured as the ratio of $^{15}N/^{14}N$ and $^{18}O/^{16}O$, and are expressed in unit of per mil (parts per thousand – $^{o}/_{oo}$). The per mil difference is the ratio difference between the sample and a reference standard material according to the following formula:

$$\delta^{15}N \text{ or } \delta^{18}O = (R_{sample}/R_{standard}) - 1) * 1000$$

$$R_{sample/standard} = {}^{15}N/{}^{14}N \text{ or } {}^{18}O/{}^{16}O$$

Kendall (1998) suggests that ^{15}N and ^{18}O of nitrate becomes heavier with a 2:1 slope due to denitrification, and that this relationship in surface and groundwater nitrate indicates the occurrence of significant amounts of denitrification in these environments. Avavena and Robertson (1998) observed this ^{15}N and ^{18}O relationship in groundwaters, but several investigators have not seen this isotopic relationship in rivers (Mayer et al., 2002; Sebilo et al., 2003). Sebilo et al., (2003) suggest that this is because benthic denitrification does not show large amounts of isotopic discrimination because the rate-limiting step is the process of nitrate diffusion through sediment. Sebilo et al., (2003) suggest that 60% of the nitrate exported from agricultural soils in the Seine River basin is eliminated in riparian buffers or through benthic denitrification.

Nitrate isotopic values can be effectively used as source tracers in aquatic environments (Showers et al., 1990, Kendall, 1998). The Neuse River Basin has numerous N inputs and the ranges of ^{15}N values at times overlap (Table 2). With the coupled use of ^{15}N and ^{18}O, NO_3^- sources can be better defined (Kendall, 1998) (Figure 8).

2.4 Estimation of Nitrogen Loads

2.4a Techniques

In-stream collection of nitrogen data can be achieved a number of ways (Table 3). The easiest and most common method is surface grab sampling from the center of the flow stream. This has been shown to be representative of average cross-sectional concentrations of nitrogen species if the water body of interest is homogenous. The United States Geological Survey (USGS) employs a method termed Equal Width Interval (EWI) sampling, whereby the width of a stream is divided into several vertical columns, which are sampled at different depths and mixed to form a representative composite sample (Green & Haggard, 2001; Hooper et al., 2001; Soerens & Nelson, 2001). Automated in-stream sampling instruments are preferred because they allow many samples to be taken at select intervals and the data retrieved later. These can be classified as either automated water samplers, which store stream samples for later processing, or in-situ analyzers (flow-injection devices, ion selective probes, or UV spectrometers), which can be left unattended for longer periods of time. Both are susceptible to spatial bias as they can only measure one point in the flow stream, but are sufficient for temporal characterization of concentration (Jordan et al., 1997; Soerens & Nelson, 2001).

Nitrogen load is defined as the mass of nitrogen carried by a body of water during a certain time period. Riverine nitrogen loads can be estimated using a variety of different techniques (Table 3). Deciding which load estimation technique to use is generally a function of the necessary sampling frequency and desired precision. Interpolation is generally agreed to be the most accurate method when intervals between samples are small (Mckee & Eyre, 2000; Soerens & Nelson, 2000; Vuorenmaa et al., 2002). However, the most common method involves relating nutrient concentration (mass/volume) or load (mass/time) to the average daily streamflow and fitting a regression line (Cohn et al., 1989; 1992; Cohn, 1995). This type of estimator requires less data and can be used to extrapolate past or future loads, whereas interpolation is only good within the measured period (Soerens & Nelson, 2001, Stow et al., 2001). Regression is dependent on a significant change in nutrient concentration with change in water flow. Phosphorus is more readily correlated with flow than nitrogen because it is tends be carried in the particulate form whereas nitrogen is mainly transported in dissolved form. In a reservoir-regulated basin with mixed input sources regression could be significantly biased on short time scales, as nutrients can be variable depending on hydrological conditions (storms or dam release). These methods are sufficient for larger rivers and streams where flow and concentration do not vary considerably between sampling intervals, however in smaller basins they may result in over or underestimation of loads (Hooper et al., 2001; Soerens & Nelson, 2001).

2.4b Neuse River Basin

A major interest in water quality in the Neuse River Basin began in the 1970's stemming from the concern of environmental impacts from the rapid population growth. This prompted the state of North Carolina to implement a statewide monitoring program in 1972 (Wilder & Simmons, 1978). Eutrophication became a concern in the early 1980's with proliferation of algal blooms, low dissolved oxygen, and fish kills (Paerl, 1983, 1987, 1995, 2002; Stanley, 1983; Christian et al., 1986; Pelley, 1998). In the last 30 years, three significant events have occurred in the Neuse Basin that have altered nutrient loading to the estuarine waters: the building of an improved wastewater treatment facility for the City of Raleigh, the Neuse River Waste Water Treatment Plant (NRWWTP) in 1976, construction of Falls Lake Dam in 1983 and the statewide ban on phosphorus detergents in 1988 (Harned, 1980; Stanley, 1988). Extreme meteorological conditions (droughts and hurricanes) in the last 10 years have enhanced the need for better short-term monitoring to detect the affects of these basin changes. A number of efforts have been made by various authors and agencies to characterize the extent to which these alterations to the system have impacted the overall health of the river and its important estuarine areas.

Harned (1980) used regression analysis of dissolved constituent concentrations versus discharge to compute annual loads from 1955-78 at USGS gauging sites at Clayton (02087500) and Kinston (02089500). By comparing monthly nitrogen concentrations in the Neuse mainstem to relatively "pristine" streams, he found the amount due to pollution contribution is over 90% in the upper basin and over 70% in the lower freshwater extent of the river. However, the Kinston USGS station does not include drainage from Contentnea Creek, believed to contribute almost one-quarter of the TN load (NCDENR, 1993).

Stanley (1988) computed inputs from non-point sources using a mass balance approach, which took into account natural processes such as nitrogen fixation and denitrification as well as fertilizer application and harvesting crops. Animal contributions were estimated using export coefficients of nitrogen waste from the populations of each type of animal. Point source estimation was derived from data provided by municipal and industrial dischargers and efficiency of sewered population output for periods prior to monitoring data (Stanley, 1988; Stow et al., 2001). Coupled with the rise in animal production and population growth, the nutrient loading in the Neuse River has changed from fertilizer to waste dominated (Stanley, 1988; Stow et al., 2001).

Dodd et al. (1992) estimated phosphorus and nitrogen inputs to the Neuse River (1989-90) by summarizing median flow and concentration from point source dischargers and land use export coefficients for all nonpoint contributions. They concluded that >75% of the nitrogen inputs were due to nonpoint sources. However, the authors acknowledged that point source input may be underestimated and the extent of basin-scale processes on coefficients was unknown (Dodd et al., 1992). These findings formed the basis for the first *Neuse River Basinwide Water Quality Management Plan* (NCDENR, 1993).

In compliance with the proposed adoption of a Total Maximum Daily Load (TMDL) for the Neuse River, the North Carolina Division of Water Quality (DWQ) evaluated nitrogen samples collected at USGS gauging sites at Kinston and Contentnea Creek at Hookerton (02091500) from 1975-95 (NCDWQ, 1999). Data were collected irregularly prior to 1985 and monthly afterward. Daily loads were calculated for each collection day and flow adjustments made using a data smoothing technique called locally weighted least squares (LOWESS) (NCDWQ, 1999). Seasonal trend analysis on nitrogen loads indicated an increasing nitrogen trend at Kinston and a decreasing trend at Hookerton. Unadjusted loads revealed no trends leading the authors to speculate that meteorological conditions were causing differing loading patterns (NCDWQ, 1999). Monitoring data for years 1991-95 allowed for a calculation of baseline loads in the Neuse over a range of different flow years. Based on those results, approximately 4.4 million kg TN yr^{-1} (4,400 metric tons N yr^{-1}) are delivered to the estuary at New Bern, NC (NCDWQ, 1999).

Stow et al. (2001) calculated nitrogen loads based on regressions of concentration to daily flow for the years 1979-98. In addition to Clayton and Kinston, the Neuse near Falls station (02087183), situated just downstream of Falls Lake Dam, was also calculated. The Clayton station showed marked overall increases in flow-adjusted total nitrogen and nitrate, while gains at Kinston in the lower basin were less pronounced.

Chapter 3 Methods

3.1 RiverNet Monitoring Program

3.1a Station Design and Locations

The RiverNet monitoring program is unique because river nutrient concentrations are measured hourly and physical parameters are measured every 15 minutes using in-situ instruments. This eliminates the problems associated with manual or automatic daily sampling and storage and permits a clearer picture of the nutrient variability inherent in a basin with multiple pollution sources. Each station consists of a WS Envirotech NAS-2E nitrate nutrient monitor (hereafter referred to as the NAS) and a physical parameter monitor (YSI 6920 sonde) housed together in a submerged aluminum cage and attached via stainless-steel cables to the center piling of a highway bridge. A 12-volt gel cell battery, continuously recharged with a solar panel, provides power to the system. A Campbell Scientific Instruments CR10x data logger and cell phone link the station to a data server at North Carolina State University, where the data are transferred every 24 hours for quality control inspection and compilation (Figure 9). Data are then posted on a website for public access (http://rivernet.ncsu.edu).

3.1b Continuous nitrate monitoring

The NAS-2E is a wet chemistry device that determines nitrate concentrations in seawater or freshwater by cadmium reduction of nitrate to nitrite (Morris & Riley, 1963; Margeson et al., 1980; Willis, 1980; Koupparis et al., 1982; Clinch & Worsfold, 1987). A cadmium column composed of 120 cm of Cd wire rolled into a Tygon tube was used. The NAS onboard chemicals were made at North Carolina State University and consisted of: 1.5L

0.4*M* NH_4Cl, 2.25L 4*M* NaCl, 250mL mixed reagent (equal parts 4 *mM* NEDD & 60 *mM* Sulphanilamide), 500mL onboard NO_3^- standard (OBS), and 250mL 300μ*M* cadmium regenerator (Regen). In addition to the OBS, nitrate calibration standards were made and verified using a Lachat QuickChem 8000 3 channel ion chromatograph. Chemicals were loaded into medical IV bags and purged of any air bubbles. The Cd column was cleaned with 50% HCl, copperized with 0.1*M* $CuSO_4$, then "activated" using a 100µ*M* NO_3^- and saltwater solution.

After software-controlled mixing sequences, in which reagents and buffers are added, the colored solution is passed through a colorimeter consisting of a green high intensity light emitting diode and silicon photodiode receiver with peak wavelength sensitivity of 560nm for nitrate (NAS manual).

$$\mathbf{D = \log (I_o / I)}$$

Where: D = Optical density of the solution

I_o = Intensity of light passing through the blank solution (volts)

I = Intensity of light passing through the colored sample solution (volts)

By comparing the optical density of the known NO_3^- concentration of the OBS to that of the sample, the nitrate concentration of the sample can be determined.

$$\mathbf{C_{Sample} = (D_{Sample} / D_{OBS}) * C_{OBS}}$$

Where: C_{Sample} = Nitrate concentration of the sample

C_{OBS} = Nitrate concentration of the onboard nitrate standard (OBS)

Samples were compared to the preceding OBS reading to determine the concentration. The OBS concentration was set at half the expected range of nitrate values, which was determined to be 0.49 ± 0.02 mg N L^{-1} in the Neuse River and Contentnea Creek. The Bear Creek site required an OBS concentration of 2.00 ± 0.02 mg N L^{-1}.

During laboratory testing, four consecutive OBS measurements were made followed by four NO_3^- sample measurements. This procedure was performed for a series of three NO_3^- standards ranging from 0.14 to 1.70 mg N L^- for Neuse and Contentnea sites and 1.00 to 3.50 mg N L^- for Bear Creek. The values calculated by the NAS had to be within 2% of the entire range of standards (~ 0.03 mg N L^{-1} for Neuse and Contentnea sites and ~0.05 mg N L^{-1} for Bear Creek) for each sample run or the cadmium column was regenerated. In field operations, an OBS standard was measured every six hours and followed by five hourly sample measurements. Based on the chemical payload requirements for hourly measurements, the NAS should be able to operate for up to four weeks (30 days) making hourly measurements without maintenance (~720 measurements, NAS manual). Deployment lengths were determined by the quality control data from each instrument downloaded daily over the cell phone network. Due to diminished data quality during high turbidity events (instrument burial) and prolonged low flow conditions in summer (OBS degradation); most deployments were on the order of three weeks (21 days).

3.1c River discharge

River depth was measured using a YSI Sonde 6920 equipped with a pressure sensor. Each pressure sensor was zeroed to the atmospheric pressure at the time of deployment. Non-vented depths in feet were recorded and corrected with static level measurements during the study. These corrections were compared to USGS gauging stations in the Neuse River Basin.

Discharge measurements were made from September 2001 to December 2002 at four of the sites and from March 2002 to May 2003 at the NRCP site. These measurements were performed at varying depth intervals and flow states (high flow, low flow, falling and rising limbs of hydrograph) to represent the observed discharge range at each station. To obtain river discharge, a 3 MHz Sontek RiverSurveyor Acoustic Doppler Current Profiler (ADCP) was used to measure the flow at each site. Morlock (1996) found ADCP's to be comparable to traditional methods of discharge measurement at USGS gauging stations for most flow ranges. The 3MHz version was rated for use in shallow water (down to 0.5m), which is common in the Neuse River during low flow. The ADCP was mounted on the front of a 14-foot Jon boat using an adjustable aluminum bracket. For shallower river stages, a smaller 12-foot Jon boat was used. Power was supplied to the unit by coupling a 12-volt gel cell battery and 6-volt wet cell motorcycle battery in series to provide 18 volts. A Trimble Geoexplorer 3 GPS receiver with a real-time differential correction Beacon-on-a-Belt (B.O.B.) was integrated into the system to provide GPS tracking capability. The GPS antenna was mounted directly above the ADCP using an adapter constructed of PVC. The ADCP and GPS receiver were connected to a laptop for data acquisition using Sontek River Surveyor software (Figure 10).

The ADCP was lowered into the water until the transducers were deep enough to remain submerged throughout the entire transect across the river (normally 0.08 to 0.24 m below water surface). High velocities, especially in the upper basin, produced some cavitation behind the unit, which required the deeper transducer setting. Two tracking options were available, bottom tracking and GPS tracking. Bottom tracking produced satisfactory results except during high discharge when the potential for bottom velocities to entrain the bed sediment (“moving bottom”) required the use of GPS to avoid a low bias to the discharge measurement (Lipscomb, 1995). Starting on one bank, a measuring rod was used to determine the edge distance from shore to the center of the ADCP transducer array. The boat was then maneuvered across the channel with the ADCP facing upstream in a heading perpendicular to the flow. The edge distance at the completion was also measured with the rod. Care was taken to maintain the lateral velocity of the boat below the downstream velocity of the water to prevent biasing the discharge. At low flow, this sometimes required that a tagline be stretched across the channel and the smaller boat pulled across by hand without the use of the motor. This procedure was repeated for a minimum of 4 transects, 2 sets of reciprocals, and the computed average was taken as the discharge. If for some reason any of the individual transects differed by more than 5 percent of the average, an additional 4 transects were taken and the average of all 8 computed for the measurement value.

Bear Creek was too shallow to use the ADCP. Average daily flows obtained from the USGS gauging station at May’s Store (0208925200), located 1.9 km downstream, were used to calculate nitrate load for the Bear Creek site, BCL. Monthly and annual discharge values were obtained from USGS gauging stations, Neuse near Falls, NC (02087183) and Contentnea Creek at Lucama, NC (02090380) to show reservoir water inputs to the Neuse River and Contentnea Creek. Daily discharge values for site NRP were computed as the sum of discharges from USGS gauging stations, Neuse near Falls and Crabtree Creek at U.S. Hwy 1 in Raleigh, NC (02087324) for that day.

3.2 Water quality

3.2a River sampling

Weekly to biweekly surface water samples were taken at the RiverNet monitoring sites to verify instrument data and provide nitrogen speciation information. In addition, sixteen other locations were sampled on the Neuse mainstem and Contentnea Creek. These were collected in the center of the flowstream by boat or by lowering a pre-washed plastic bucket from the top of a highway bridge. Samples were then placed into pre-washed (10% HCL rinsed) 4L polyethylene cubitainers and transported inside a cooler to the lab. Within 24 hrs of collection, each sample was filtered through a Whatman GFF 0.7micron filter and kept in a dark cold room until analyzed.

Filtered samples were processed using a Lachat QuickChem 8000 3 channel ion chromatograph. Nitrite plus nitrate given as nitrate (NO_3-N) was determined using the cadmium reduction method (EPA Method 353.2, U.S. EPA, 1983). Total Kjeldahl nitrogen (TKN), composed of NH_4^+ (EPA Method 350.1, U.S. EPA, 1983) plus dissolved organic nitrogen (DON), was determined by the digestion method (EPA Method 351.2, U.S. EPA, 1983). Dissolved inorganic nitrogen (DIN) was defined as sum of NO_3^--N and NH_4^+. The total dissolved nitrogen (TDN) fraction was used for this study and was defined as the sum of DIN and DON.

3.2b Spatial analysis

Since RiverNet instrumentation measures a single point within the flowstream, a spatial bias may occur if the river is not evenly mixed laterally and vertically (Tonderski et al., 1995; Stalnacke et al., 1999; Soerens & Nelson, 2000). It is generally accepted that sample collection using depth and equal width integration (EWI) techniques is more representative of the cross-sectional streamflow than collection at a single point (Wilde et al., 1999). The Neuse River, Contentnea Creek and Bear Creek were believed to be spatially homogenous in NO_3^- concentration due to their small cross-sectional areas. EWI sampling was conducted at Fort Barnwell (NRB) and depth sampling at Grifton (CCG) during average flow states to verify these assumptions. A sampler constructed of PVC pipe, equipped with a sonde and a peristaltic pump, was lowered in the stream to sample different depths. Three vertical sections at NRB and one at CCG were sampled to a depth of 2 m.

3.2c Nitrate isotopic determination

One to four liters of sample was enough water to yield 15μM of nitrogen, which was passed through a double ion exchange resin column (1st - cation - 5 ml Biorad AG 50-WX8; 2nd - anion - 2ml Biorad AG 2-X8). The cation column was pre-washed with deionized water (DI), the anion column was pre-washed with 3N HCL, and then repeatedly washed with DI water to remove all acid residues. Pre-washing the anion column with the same strength acid as the elutant allows dissolved samples 15μM in size to be analyzed without an isotopic correction (Chang et al. 1999). Nitrate was eluted from the anion column with 30 ml of 3N HCl. The HCl was neutralized with 15g of Ag_2O, the sample was filtered with a Whatman GFF filter, and the filtrate was freeze dried to yield a fine white powder $AgNO_3$. Half the sample was placed in a tin boat and combusted in a Carlo Erba NC2500 Elemental Analyzer and isotopically analyzed with a Finnigan Mat Delta+ XLS CF-IRMS to determine $\delta^{15}N$-NO_3^-. The other half of the sample was placed in a silver boat and pyrolyzed with a Thermoquest Thermal Conversion Elemental Analyzer (TCEA) and isotopically analyzed with a Finnigan Mat Delta+ XL CF-IRMS to determine $\delta^{18}O - NO_3^-$. The $\delta^{15}N$ results were calibrated against NIST 8550, NIST 8548, NIST 8547, and four internal ^{15}N standards. The $\delta^{18}O$ results were calibrated against NIST 8542, 8549, NBS 120c, NBS 127, and two internal ^{18}O standards. Results are expressed as per mil deviations from the international standard according to the following formulas:

$\delta^{15}N = \{(^{15}N/^{14}N_{sam} / {}^{15}N/^{14}N_{std}) - 1\} * 10^3$ $^{15}N/^{14}N_{std}$ = Atm N_2 (Mariotti, 1983)

$\delta^{18}O = \{(^{18}O/^{16}O_{sam} / {}^{18}O/^{16}O_{std}) - 1\} * 10^3$ $^{18}O/^{16}O_{std}$ = VSMOW (Vienna Std Mean Ocean Water)

Chapter 4 Statistical Methods

4.1 Depth-Discharge Derivation

Discharge measurements made by the ADCP were related to station depth to form site-specific depth-discharge relationships. The logarithmic method was chosen for calculation of the discharge equation due to its simplicity (straight line) and ability to be extrapolated outside of the measured discharge and depth range (Kennedy, 1983; Herschy, 1995). The equation is in the form:

$$\log Q = \log C + n \log (h + a)$$

Where: Q = Discharge (m^3s^{-1})

h = Depth (m)

a = Correction factor for the depth of the river at zero flow (m)

C & n = Constants derived from a log-log plot of discharge versus depth

Factoring out the logarithms, yielded the following depth-discharge equation:

$$Q = C (h + a)^n$$

The correction factor, *a*, was determined experimentally from the maximum ADCP depth of the channel in relation to the station's depth in the river cross-section. The *standard error of estimate* (S_e) for the depth-discharge relationship is given by:

$$\mathbf{S_e = [\Sigma d^2 / (N-2)]^{0.5}}$$

Where: d = Deviation of an ADCP measurement from the calculated value from the depth-discharge regression

N = Total number of ADCP measurements

Student's t values are needed to correct for small sample sizes (< 20 measurements), therefore, the 95% confidence interval of scatter about the regression is given by, tS_e (Herschy, 1995). Based on sample sizes (N = 10 - 11 measurements), a Student's t value of 2.2 was chosen for all sites except NRB. A Student's t value of 2.0 was used at NRB due to its larger sample size (N= 20; 11 RiverNet and 9 USGS measurements). The uncertainty of estimates of discharge from the depth-discharge equation is determined by calculation of the *standard error of the mean relation* (S_{mr}) for the 95% confidence interval. This gives minimum error at the mean value of the regression and maximum at the upper and lower limits (Herschy, 1995).

4.2 Nitrate Load Calculation and Nitrogen Flow-Normalization

Nitrate loads were calculated by linear interpolation of hourly nitrate concentrations to a quarter-hour time step and multiplication by the total discharge in the interval between samples (McKee and Eyre, 2000). The equation is given as:

$$\mathbf{L = CQ_{int}}$$

Where: L = NO_3^- load (kg)

C = NO_3^- concentration (kg m^{-3})

Q_{int} = Discharge in the time interval between NO_3^- concentrations (m^3)

Daily, monthly and yearly NO_3^- loads were computed for each continuously monitored RiverNet site. Flow-weighted annual mean NO_3^- concentrations were determined by dividing total NO_3^- load by discharge at each RiverNet site. Due to lack of significant concentration to flow relationships at all sites, water samples were not weighted with respect to flow.

Chapter 5 Results

5.1 River Discharge

Depth-discharge relationship plots are shown in Figures 11-13. At least ten measurements were made at each continuous monitoring site except BCL, which was not measured due to access problems and the presence of a USGS gauge immediately downstream from the site (Appendix A). Instrument cages were placed along center bridge pilings, which coincided with the deepest points of the river cross-section at most sites. Depth correction factors were needed for the two Contentnea sites, CCH (a= +0.24) and CCG (a= -1.17). The equations generated were deemed to be good representations of the flow conditions encountered during the period of study due to the large percentage of discharge range measured with the ADCP (Table 4). Site NRCP, in which only 46% of the discharge range was covered, was primarily due to one extremely large storm event occurring in October 2002 (days 284-286). Excluding this event, a discharge range of 161 m^3s^{-1}

(2 - 163 m^3s^{-1}) at the site would result in 70% discharge coverage. The two RiverNet sites, NRB and CCH, which were co-located with USGS gauging stations had <60% discharge coverage.

Annual discharge totals and water yields were consistent at all sites for 2001 and 2002 (Table 5). Sites located immediately downstream of reservoirs (FL and CCW) had the lowest water yields, while BCL, located in a small agricultural basin, had the highest yield during the study. The period from May 2002 to May 2003, when BCL was continuously monitored, had slightly higher water yield than either of the two calendar years due to increased rainfall in the winter and spring of 2003. Monthly discharge variations were observed at all sites with the highest discharge occurring during the winter and spring seasons (Figure 14).

The USGS gauging station at Fort Barnwell (02091814) measures discharge using a velocity relationship instead of depth-discharge. This is due to astronomical and wind tides affecting the flow (USGS, 2002). In addition, overflow channels on both sides of the river upstream of the station divert some flow during high discharge events resulting in calculated discharge below actual conditions. Overflow became prevalent at a Fort Barnwell RiverNet station depth of 2.90 - 3.05m or 104 - 116 m^3s^{-1} (Caldwell, USGS, personal communication). In order to eliminate these problems, average daily flows from the USGS gauging station were used for load calculations at site NRB. USGS daily flow values were also used for site BCL. Similarly, quarter-hourly data from the USGS gauging station at Hookerton (02091500) was used in place of RiverNet (CCH) calculated discharge to allow discharge comparison for the entire 2001 calendar year. RiverNet underestimated annual discharge totals at CCH by only 3.2% and 7% at NRB compared to the USGS gauging stations (Figure 15).

5.2 Nitrate Variability

Nitrate concentrations were variable at all sites, but the variability generally diminished downstream away from large point sources (Figs. 16-18). Upper basin sites are prone to rapid fluctuations in discharge and nitrate (i.e. hourly) due to relatively narrow channels and large input of urban runoff. The lack of such dominant point sources in the lower basin allows more uniform nitrate concentrations with smaller variations resulting from gradual responses to changing flow conditions.

Nitrate concentrations in surface samples measured by the Lachat compared favorably to the values determined by the NAS at depth and were statistically significant ($p<0.05$) (Figures 19-21). The strongest correlations were found at CCH (N=25; $R^2=0.94$; $p<0.0001$), NRB (N=41; $R^2=0.92$; $p<0.0001$), and BCL (N=21; $R^2=0.92$; $p<0.0001$). The two upstream Neuse sites: NRCP (N=38; $R^2=0.63$; $p<0.0001$) and NRSS (N=36; $R^2=0.68$; $p<0.0001$), as well as the lower Contentnea site, CCG (N=38; $R^2=0.62$; $p<0.0001$), were subject to outlier values that diminished the fit of the data to the linear regression.

EWI sampling was conducted in September 2002 at NRB during an instantaneous flow of 91 ± 1 m^3s^{-1}, slightly larger than the 2002 mean daily flow (73 m^3s^{-1}). A total of three vertical depth sections within the water column spaced equally from the center and covering the middle 55% of the river cross-section (total width of river at time of sampling = 100m) were sampled. Three water samples were taken from the center parallel (depth intervals= 0.1, 1.0, and 2.0 m) and one each from the side parallels (depth = 1.6 m). Results indicate almost no variation in NO_3^- (Mean = 0.40 $\pm$ 0.01 mg N L^{-1}; Range: 0.39 to 0.41 mg N L^{-1}; N=5), little variation in NH_4^+ (Mean = 0.05 $\pm$ 0.01 mg N L^{-1}; Range: 0.04 to 0.07 mg N L^{-1}; N=5) and some difference in DON (Mean = 0.77 $\pm$ 0.12 mg N L^{-1}; Range: 0.64 to 0.95 mg N L^{-1}; N=5). The NO_3^- value measured at the RiverNet station was 0.40 $\pm$ 0.03 mg N L^{-1} during the time of sampling. In Contentnea Creek, river samples were taken from a centrally located, vertical depth parallel (depth intervals = 0.2, 0.7, and 2.0 m) at CCG in May 2002 during a time of low instantaneous flow (2.2 $\pm$ 0.2 m^3s^{-1}). Results again verified the assumption of homogeneity of dissolved nitrogen species concentrations across the stream: NO_3^- (Mean = 0.44 $\pm$ 0.01 mg N L^1; all samples equal; N=3), NH_4^+ (Mean= 0.03 $\pm$ 0.02 mg N L^{-1}; Range: 0.01 to 0.05 mg N L^{-1}; N=3), and DON (Mean = 1.03 $\pm$ 0.08 mg N L^{-1}; Range: 0.91 to 1.11 mg N L^{-1}; N=3).

5.3 Nitrate Loading

Annual NO_3^- loads were similar for both monitored years at sites with complete records (Table 6). Flow-normalized annual NO_3^- concentrations and NO_3^- yields varied little between Neuse and Contentnea sites, but were considerably higher at the agriculturally-dominated site, BCL (Table 6). Monthly NO_3^- loads in the Neuse River Basin displayed similar patterns to discharge with high NO_3^- load months coinciding with winter/spring high discharge months (Figures 22 – 24). Decreasing monthly NO_3^- concentrations were observed at all sites except for BCL where an increasing concentration trend occurred. Mass balance of NO_3^- load and discharge in three reaches between RiverNet monitoring sites show the NO_3^- concentration of the added discharge is considerably different in the Upper Neuse compared to the Lower Neuse and Contentnea Creek (Table 7).

Linear regressions of NO_3^- load to mean daily NO_3^- concentration and mean daily discharge indicate discharge to be a more important factor in predicting NO_3^- load than concentration (Figures 25 – 30). All Neuse and Contentnea sites displayed strong correlations between NO_3^- load and mean daily discharge ($R^2 \geq 0.69$; $p<0.0001$) but not NO_3^- load and mean daily NO_3^- concentration ($R^2 < 0.03$). However, the regressions for NO_3^- load and mean daily NO_3^- concentration were found to be statistically significant ($p<0.05$) at all sites except NRSS ($p = 0.07$). BCL, located in the predominantly agricultural watershed had the highest correlations for NO_3^- load to mean daily discharge ($R^2 = 0.91$; $p<0.0001$) and NO_3^- load to mean daily NO_3^- concentration ($R^2 = 0.35$; $p<0.0001$).

Daily NO_3^- loads based on only one NO_3^- sample per day taken at 12 noon can result in > $\pm$ 60% difference from hourly monitoring (Figure 31). The difference became less pronounced on a monthly time step as NO_3^- loads varied only $\pm$ 10% at all sites except NRCP, which was $\pm$ 20%. Annual NO_3^- loads were within + 5% at all sites.

The City of Raleigh Public Utilities Division (CORPUD) operates the Neuse River Waste Water Treatment Plant (NRWWTP), which is located 2.5 km upstream of the NRCP site. Treated effluent release has a significant effect on water discharge and NO_3^- load at the site during low flow conditions (Figure 32). The NRWWTP on average discharged 1.4×10^5 m^3d^{-1} during the study period even though it is permitted for a maximum discharge allowance of 2.3×10^5 m^3d^{-1} (CORPUD, unpublished data). Falls Lake release accounted for up to 80% of the monthly NRCP water discharge during the study period, while NRWWTP accounted for a maximum of 24% during the lowest discharge month (November 2001). Monthly NO_3^- loads at NRCP indicate during low discharge months, >100% of the total NO_3^- load may originate from NRWWTP (CORPUD, unpublished data). During the period of record, Falls

Lake contributed approximately 45% of the discharge, while NRWWTP only 7% of the discharge measured at NRCP. However, 45% of the NO_3^- load at NRCP was delivered by the NRWWTP due to the large NO_3^- content in its effluent (Mean NO_3^- = 2.72 mg N L^{-1}) compared to Falls Lake (Mean NO_3^- = 0.12 mg N L^{-1}).

5.4 Nitrogen Analyses

5.4a Speciation

Analysis of water samples collected during 2001-02 revealed distinct nitrogen speciation trends in the Neuse Basin (Table 8). Sampling sites located immediately downstream of reservoirs (FL, NR1, BCS, & CCW) had the lowest average NO_3^- concentrations ($\leq$ 0.17 mg N L^{-1}) and TDN concentrations ($\leq$ 0.83 mg N L^{-1}). Excluding the agricultural site BCL (NO_3^- = 2.32 $\pm$ 0.60; TDN = 3.02 $\pm$ 0.56 mg N L^{-1}), the highest NO_3^- and TDN concentrations were found at the second station (NRC-42 - station 5) downstream from the NRWWTP (Figure 33). Concentration trends in Contentnea Creek were similar to the Neuse mainstem with NO_3^- and TDN concentrations maintaining relatively constant levels below major urban input sources (Figure 33). Most of the smaller tributaries sampled were impounded to some degree therefore concentrations were diminished. However, Middle Creek (sites MCC & MCS) exhibited the effect of point source impact from the Cary South WWTP (4.8×10^4 m^3 day^{-1} permitted discharge) with NO_3^- and TDN concentrations comparable to the Neuse mainstem and Contentnea (Figure 34).

DON was the dominant dissolved nitrogen species at most sites, ranging from 0.53 to 0.82 mg N L^{-1} in the basin. NH_4^+ concentrations were very low, reaching maximum concentrations at site BCL and immediately downstream of reservoirs and ranging from 0.03 to 0.17 mg N L^{-1}.

5.4b Isotopes

Median $\delta^{15}N$ values in the Neuse River Basin indicate sites above the NRWWTP fall within the soil NO_3^- (+4 to +9) and precipitation (-14 to +15) ranges (Figure 35). NRCP, NRS-1201, NRSS, & MCC, exhibit elevated $\delta^{15}N$ values in the point source range (+11 to +35) as well as larger variability about the median. Mixed source sites and BCL fall between the urban sites in terms of $\delta^{15}N$ values. The proliferation of hog lagoons within the Bear Creek watershed elevates the $\delta^{15}N$ value at site BCL above that of other agricultural drainages studied within the basin (Showers et al., 1990). At high flow, values move toward soi1 NO_3^- and/or precipitation. The use of dual isotopes $\delta^{18}O$ and $\delta^{15}N$ of NO_3^- has been shown in previous studies to be effective in NO_3^- source determination as well as indicating if denitrification has occurred (Kendall, 1998). Results from 2001-02 in the Neuse River Basin do not indicate clear denitrification trends (Figure 36).

$\delta^{15}N$ (per mil) values are dependent on major source inputs and the proximity to these sources (Kendall, 1998). Site NRP, an urban location upstream of the NRWWTP, showed little variation in NO_3^- concentration or $\delta^{15}N$ with increasing discharge, while site NRCP below the NRWWTP input showed decreases in both NO_3^- concentration and $\delta^{15}N$ with increasing discharge (Figure 37). Although few samples were collected at high discharge, the agricultural site BCL displays little variation in $\delta^{15}N$ with increasing discharge and NO_3^- concentration tends to increase with flow. NRB and other mixed source sites exhibit decreasing $\delta^{15}N$ but variable NO_3^- concentrations with increasing flow (Figure 38).

Chapter 6 Discussion

6.1 River Discharge

The water released from Falls Lake constituted 21% of the total annual discharge flowing past NRSS and 15% of the discharge past NRB in 2001. Contributions of Falls Lake outflow to total discharge past NRCP, NRSS, and NRB during 2002 were 47, 23, and 15% respectively. Discharge at NRCP was further broken down to account for contributions from NRWWTP and Crabtree Creek, the largest tributary between the Falls Lake and the monitoring site. During calendar year 2002, these 3 inputs accounted for 74% of the total flow at the NRCP site (Falls Lake 47%; Crabtree 20%; NRWWTP 7%). Between NRCP and NRSS, most of the additional discharge is explained by the input of tributaries and groundwater. Middle (MCS), Swift (SCS), and Black Creeks (BCS) add approximately 8%, while Little River (LRG) accounts for 11% of the total discharge at NRSS. NRB, which is located just below the confluence of Contentnea Creek, was broken down into percentage of flow from the Neuse mainstem (NRK) and Contentnea Creek (CCG). Discharge totals for 2001 and 2002 were (77 and 70% NRK; 26 and 27% CCG). The combined yearly totals are $\pm$3% of the totals measured at NRB. Stream flow differences of up to 5% along a river reach can be explained by hyporheic exchange (Hinkle et al. 2001). Tritium (^3H) values in the lower Neuse basin indicate that three-fourths of the water is less than one year old, which tends to support the relative lack of significant deep groundwater exchange (Michel, 1992).

6.2 Nitrate Loading

6.2a Nitrate Loads

Nitrate loads computed by linear interpolation were comparable to other studies within the Neuse Basin during similar low discharge years (Stow et al, 2001; Stow and Borsuk, 2003). Nitrate loads were very consistent throughout the basin over the two years of monitoring. The highly urbanized Upper Neuse (site NRCP) was found to have the highest flow-normalized annual concentration (0.50 ± 0.08 mg N L^{-1}) as well as the largest NO_3^- yield (130 ± 21 kg N km^{-2}) in the Neuse River mainstem, just below the NRWWTP (Table 6). NRSS was found to have a smaller load per drainage area and subsequently has a lower annual concentration and yield. The total NO_3^- load for the RiverNet monitoring area (site NRB) was computed to be 11×10^5 kg N for both 2001 and 2002. Due to the lack of discharge, this value should be considered a lower bound for NO_3^- loading. All three mainstem sites display decreasing monthly flow-normalized concentrations although with poor correlation coefficients.

Contentnea Creek has historically been linked to high nitrogen loading. As a USGS NASQAN site, CCH has the highest nitrogen total in the Albemarle-Pamlico study area (Harned et al., 1995). The 2002 NO_3^- load at CCH was $2.2 \pm 0.3 \times 10^5$ kg N, comparable in NO_3^- yield and concentration to the CCG site downstream. The 2.8 and 2.9×10^5 kg N measured at site CCG in Contentnea Creek during 2001 and 2002 corresponds to more than one-quarter (26-27%) of the total NO_3^- load measured for the RiverNet study area at NRB (11×10^5 kg N). This percentage is comparable to the Neuse River Basinwide Management Plan value (NCDENR, 1993).

The Bear Creek, site BCL, located in a agriculture dominated watershed (67% land use) had the highest NO_3^- yield of any RiverNet monitored site (820 $\pm$ 120 kg N km^{-2}). DIN composed over 82% of the TDN, comparable to other small Coastal Plain watersheds where land use is more than 40% agricultural (Jordan et al., 1997). Channelized runoff in tile drains from fertilized fields enhances nitrogen delivery into receiving streams by bypassing natural flowpaths (Jacobs & Gilliam, 1983; Lowrance, 1992). Nitrate concentrations above 10 mg/L were not uncommon in drainage ditches in the watershed (USGS, 2002; 2003). This influence was reflected in the creek, resulting in the highest flow-weighted concentrations occurring during the months of greatest discharge. In addition, many CAFO's are also located within the watershed. The creek is fed by nitrate-rich groundwater during baseflow conditions resulting in NO_3^- concentrations greater than 1.0 mg/L throughout the study period, (Stoddard, 1994).

6.2b Controls

Based on the regressions in Figures 25 – 30, water discharge appears to be driving factor in NO_3^- loading during low discharge years. Drainage area also is a factor as many small basins export more NO_3^- per unit area due to the greater water yield. Groundwater and surface drainage flow paths become longer with the increased basin size and low precipitation, which in turn can lead to greater landscape loss (Alexander et al., 2000). The only site that displayed any NO_3^- concentration relationship to NO_3^- load was BCL (R^2 = 0.35; p<0.0001). This was most likely due to the lack of dilution during storm events because of the large agricultural runoff and contaminated groundwater discharge.

Mass balances were computed for three river reaches to attempt to determine whether NO_3^- loading between RiverNet sites was due to tributary surface water inputs or groundwater discharge (Table 7). The mean NO_3^- concentration (0.34 mg N L^{-1}) computed from the changes in NO_3^- load and discharge; reveal that the nitrate concentration in the water input between NRCP and NRSS is relatively low in NO_3^- compared to the concentration of the river. Tributaries sampled within this reach have NO_3^- concentrations of 0.08 to 0.35 mg N L^{-1}. This indicates that possibly tributary inputs are responsible for the NO_3^- difference between the two sites. The second reach is between NRSS and NRB, from which a NO_3^- value of 0.61 mg N L^{-1} for the incoming water is derived. Bear Creek is located within this reach and is predominately groundwater fed with mean NO_3^- concentration over 2.00 mg N L^{-1}. Contentnea Creek also enters this reach, so the groundwater nitrate input is probably significant as well as overland flow. The third reach is between the two Contentnea sites CCH and CCG. The only major inflow between the two sites is Little Contentnea Creek, which receives effluent from a small NPDES discharger (Farmville Town WWTP). Sampling performed by the USGS in Little Contentnea Creek during the study period revealed very low nitrate concentrations (USGS, 2002). Mean NO_3^- concentration of the reach's water input is 0.45 mg N L^{-1}, very similar to the level found in the creek at each site.

6.2c Sampling frequency

Taking one NO_3^- concentration sample per day at 12pm, can result in large daily NO_3^- load estimation errors (up to $\pm$ 60%) at all sites downstream of NPDES dischargers (Figure 31). BCL was the lone exception at $\pm$ 20% error. However, on monthly time scales, sampling once per day will only give errors up to 17% at sites NRSS, NRB, CCH, CCG, and BCL.

NRCP was ± 25% on the monthly timescale. Annual errors associated with taking one sample per day were less than ± 5% at all sites. The shorter the time frame, the more samples needed to accurately characterize the NO_3^- load variability.

6.3 Nitrogen Speciation

DIN and TDN steadily increase downstream of Falls Lake, reaching a maximum at Station 5 (NRC-42) (Figure 37). A gradual decline until Station 8 (NRS-1201) is observed before finally stabilizing in the lower basin. An explanation for this decrease is the presence of wetlands between the cities of Smithfield and Goldsboro. These areas have the potential for denitrification (Jacobs & Gilliam, 1983; Johnston, 1991; Seitzinger, 1988; Howarth et al., 1996). Swift, Middle and Black Creeks also enter the Neuse mainstem upstream of NRS-1201 and Little River connects downstream. Sites on these creeks (SCC, SCS, MCC, MCS, BCS, and LRG) indicate decreasing NO_3^- and NH_4^+ concentrations as they near the mainstem. Coupled with a decrease in population density, decrease in wastewater effluent, and increase in basin drainage area, nonpoint source inputs may become more significant. Transport from these sources is heavily dependent on discharge and atmospheric deposition, which was diminished due to low precipitation during the study period. In smaller watersheds, TDN is positively correlated with runoff (Lewis, 2002).

Howarth et al. (1996) estimate the average annual TDN yield from the region to be greater than 600 kg N km^{-2}. Smith et al. (1997) estimate the probable TDN yield in the Neuse River Basin to be 500-1000 kg N km^{-2} in the upper and middle basin and > 1000 kg N km^{-2} in the lower basin. These values are based on limited sampling (monthly) and average conditions over many years. Climatic fluctuations can alter nutrient delivery on shorter time scales (Mckee and Eyre, 2000; Justic et al., 2003). TDN estimated at site NRB for 2002, based on continuous NO_3^- monitoring and mean values for DON (0.73 mg N L^{-1}) and NH_4^+ (0.04 mg N L^{-1}) would be 29 x 10^5 kg N yr^{-1}. The TDN yield for the RiverNet monitoring area is 285 kg N km^{-2}. This low flow estimate of TDN yield is well below the previous estimates of Howarth et al. (1996) and Smith et al. (1997), indicating that the drought conditions that persisted through the study period have dramatically affected nutrient delivery in the Neuse River Basin.

6.4 Isotopic Analysis

Showers et al. (1990) demonstrated a strong relationship between $\delta^{15}N$ and discharge in the lower Neuse River. Site NRP located in an urban setting above a major NPDES discharger (NRWWTP), NRCP in an urban location immediately below the NRWWTP, BCL located in a predominately agricultural and CAFO influenced watershed, and NRB the lowermost site in the RiverNet monitoring area were chosen. $\delta^{15}N$ and NO_3^- were plotted against mean daily discharge and fitted with power functions (Figures 37 & 38).
The strongest NO_3^- correlations were found at BCL (R^2 = 0.50) the site most likely to be influenced by flow. NO_3^- concentrations at BCL were positively affected by agricultural runoff at high discharge. The strongest $\delta^{15}N$ was not in the lower basin as in previous research, but at the NRCP site downstream of the NRWWTP (R^2 = 0.48). Elevated $\delta^{15}N$ emanating from the NRWWTP are diluted at high discharge.

Chapter 7 Conclusion

Extreme drought conditions during the study provided a unique opportunity to examine the lower bounds of nitrogen delivery in the Neuse Basin. Results from the first two years of RiverNet monitoring in the Neuse River basin reveal:

1. In-stream monitoring of NO_3^- concentration and discharge provide an efficient way to characterize water quality with minimal amount of field sampling.
2. Temporal NO_3^- concentration variability was found to be much larger than spatial variability.
3. Site NRCP showed the greatest amount of hourly NO_3^- concentration variability resulting from its location downstream of the largest NPDES discharger in the basin.
4. Taking only one NO_3^- concentration sample per day can induce daily NO_3^- load errors of up to $\pm$ 60 % at sites affected by wastewater effluent, however this error becomes less significant on monthly or annual time scales.
5. The DIN percentage of total dissolved nitrogen increases with distance downstream from the Falls Lake Reservoir (23 $\pm$ 21% DIN) due to urban runoff and wastewater input (RWWTP), reaching a maximum of 58 $\pm$ 12% at NRC-42. The percentage of DIN then gradually decreases in the lower basin to 42 $\pm$ 11% at NRB. Contentnea Creek DIN was found to be similar to the Neuse mainstem with DIN increasing from the impoundment in the upper basin and reaching a maximum percentage at CCG (44 $\pm$ 11% DIN).
6. Total dissolved nitrogen in smaller tributaries was highly variable with agricultural watersheds (>60% cropland) largely composed of DIN (BCL = 82 $\pm$

8% DIN) and forested watersheds relatively depleted in DIN (MCS = 38 $\pm$ 14% DIN).

7. Nitrate loads calculated by interpolation of concentration and discharge data show little annual variability at NRB (2001 = 11 $\pm$ 1.0 x 10^5 kg N yr^-; 2002 = 11 $\pm$ 1.0 x 10^5 kg N yr^-) with CCG (2001 = 2.8 $\pm$ 0.5 x 10^5 kg N yr^-; 2002 = 2.9 $\pm$ 0.5 x 10^5 kg N yr^-) accounting for approximately one-quarter (26 %) of the total load in the monitored portion of the Neuse Basin.
8. Flow-normalized annual NO_3^- concentrations at continuously monitored sites during the 2002 calendar year showed little difference in the Neuse mainstem (0.42 $\pm$ 0.08 mg N L^{-1} to 0.50 $\pm$ 0.08 mg N L^{-1}) and almost no difference between the two Contentnea sites (both $\simeq$ 0.46 $\pm$ 0.08 mg N L^{-1}).
9. All mainstem sites were located downstream of the largest NPDES discharger in the basin, the Neuse River Waste Water Treatment Facility. Contentnea sites were also downstream of major NPDES discharge. High-resolution monitoring is necessary at sites dominated by NPDES discharge to accurately characterize temporal NO_3^- variability during low flow. Agriculturally dominated watersheds or those that contain large numbers of CAFO's, are less prone to NO_3^- concentration fluctuations during low flow conditions but may have high background NO_3^- concentrations due to groundwater contamination.
10. Use of generalized nitrogen yields based on large-scale regional analysis may not reflect local conditions due to climatic events such as droughts. NO_3^- yields in the Neuse River mainstem and Contentnea Creek were 99 - 130 kg N km^{-2}. Bear Creek's NO_3^- yield from May 2002 to May 2003 was 820 $\pm$ 120 kg N km^{-2}. TDN

yield for the RiverNet Monitoring area was estimated to be 285 kg N km^{-2}, well below previous estimates.

Isotopic analyses of nitrate ($\delta^{15}N$ and $\delta^{18}O$) have been used by a number of authors to indicate denitrification within waterways but provide little evidence for such occurrence in the Neuse River Basin (Kendall, 1998; Kendall & Aravena, 2000; Kendall & Coplen, 2001). $\delta^{15}N$ and NO_3^- at sites dominated by wastewater show decreasing trends during high daily discharge periods. Agricultural sites, as was the case with BCL, show decreasing $\delta^{15}N$ values with discharge, however NO_3^- concentrations also increase with discharge. Mixed source sites display decreasing $\delta^{15}N$ values but variable NO_3^- concentrations with increased discharge.

Future research should focus on isolating changes in speciation from perceived reductions based on nitrate analysis only. Atmospheric deposition is believed to be a major nutrient input in the middle and lower basin with a large portion of the N composed of NH_4^+. Also, the bioavailability of DON is not quite understood and could be a factor in eutrophication, although DON concentrations found in this study were mostly constant throughout the basin. Monitoring through changing discharge years and implementation of RiverNet stations in small watersheds of varying land usage should also help clarify nutrient loading and N loss mechanisms. If a 30% reduction in nitrogen is desired as mandated by the NC Legislature in 2001, then adequate sampling programs must be developed that take into account proximity to nutrient sources. In determining the effectiveness of management strategies aimed at curbing nutrient delivery to estuarine waters, the RiverNet program will facilitate detection of such trends.

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Table 1. RiverNet sampling locations 2001-02.

Map #	Station Name	RiverNet ID	Latitude N	Longitude W	Drainage (km^2)	Downstream Distance (km)
	NEUSE MAINSTEM					
1	Neuse River at Falls	FL	35° 56' 26.30"	78° 34' 47.64"	1997	0.0
2	Neuse River at US Hwy 1 (Raleigh)	NR1	35° 54' 32.16"	78° 33' 17.11"	2051	5.3
3	Neuse River at Poole Road (Raleigh)	NRP	35° 45' 16.33"	78° 31' 55.68"	2650	29.8
4	Neuse River at Clayton (Mial Plantation Rd)	NRCP	35° 42' 08.53"	78° 28' 41.52"	2841	40.1
5	Neuse River at Clayton (Hwy 42)	NRC-42	35° 38' 50.75"	78° 24' 19.44"	2978	51.8
6	Neuse River at Smithfield (70 Bus.)	NRS-70	35° 30' 46.01"	78° 20' 58.60"	3124	68.5
7	Neuse River at Smithfield (Hwy 301)	NRS-301	35° 28' 54.12"	78° 22' 09.80"	3950	74.4
8	Neuse River at SR 1201	NRS-1201	35° 22' 26.73"	78° 11' 46.28"	4481	107.9
9	Neuse River at Goldsboro (Hwy 111)	NRG	35° 15' 41.10”	77° 54' 38.17"	6345	178.3
10	Neuse River at Seven Springs	NRSS	35° 13' 45.05"	77° 50' 46.68"	6400	191.8
11	Neuse River at Kinston	NRK	35° 15' 32.26"	77° 35' 00.60"	6972	245.3
12	Neuse River at Fort Barnwell	NRB	35° 18' 45.18"	77° 18' 08.64"	10132	267.8
	TRIBUTARIES					
13	Swift Creek at Clayton	SCC	35° 36' 47.40"	78° 32' 57.52"	224	----
14	Swift Creek at Smithfield	SCS	35° 31' 07.07"	78° 22' 53.42"	401	----
15	Middle Creek at Clayton	MCC	35° 35' 11.51"	78° 39' 18.31"	216	----
16	Middle Creek at Smithfield	MCS	35° 30' 27.80"	78° 24' 05.58"	335	----
17	Black Creek at Smithfield	BCS	35° 28' 09.24"	78° 27' 25.35"	256	----
18	Little River at Goldsboro	LRG	35° 24' 11.06"	78° 01' 16.06"	818	----
19	Contentnea Creek at Wilson	CCW	35° 41' 16.80"	77° 56' 52.08"	614	0.0
20	Contentnea Creek at Hookerton	CCH	35° 25' 42.96"	77° 34' 57.72"	1898	82.4
21	Contentnea Creek at Grifton	CCG	35° 22' 11.82"	77° 26' 45.60"	2538	108.4
22	Bear Creek at LaGrange	BCL	35° 17' 16.01"	77° 48' 12.24"	127	----

Table 2. $\delta^{15}N$ range values for nitrogen sources in the Neuse River Basin.

Nitrogen Source	$\delta^{15}N-NO_3$ Range	Reference
WWTP with Biological Denitrification	+15 to +35	Showers in press
Animal Waste	+15 to +20	Karr et al. (2001; 2002; 2003)
	+10 to +20	Kreitler (1979) Wassenaar (1995)
WWTP without Biological Denitrification	+11 to +18	Showers et al. (1990) Showers in press
Soil Nitrate	+4 to +9	Heaton (1986)
Agricultural drainage	+6 to +9	Showers et al. (1990)
Precipitation	-5 to +10	Kendall (1998)
	-14 to +15	Showers in press

Table 3. Literature review of nitrogen load estimation techniques.

Authors	Location	Sample Frequency	Collection Method	Load Estimation
Stalnacke et al. (1999a)	Swedish Rivers	Monthly	Discrete sample	Linear interpolation
Hooper et al. (2001)	US large rivers	Monthly and storm	Discrete sample	Regression
Stalnacke et al. (1999b)	Baltic Rivers	Weekly to quarterly	Discrete sample	Linear interpolation
Jordan et al. (1997)	Chesapeake Bay, USA	Weekly and Storm	Automated water sampler	Mean conc. and flow
Sprague (2000)	Chesapeake Bay, USA	Semi-monthly and storm	Discrete sample	Log-linear regression
Soerens & Nelson (2000)	Illinois River, USA	Bi-weekly and storm	Automated sampler and discrete	Linear interpolation
Green & Haggard (2001)	Illinois River, USA	Bi-monthly and storm	Discrete sample	Log-linear regression
Mckee & Eyre (2000)	Australia	Monthly and storm	Discrete sample	Linear interpolation
Prego & Vergara (1998)	Spain	Monthly	Discrete sample	Regression
Vanni et al. (2001)	Ohio-Indiana, USA	Monthly and storm	Automated water sampler	Regression
Vuorenmaa et al. (2002)	Finland	Bi-weekly and storm	Automated water sampler	Interpolation
Arheimer et al. (1996)	Sweden and Finland	Monthly	Discrete sample	Regression
Christensen (2001)	Rattlesnake Creek, KS, USA	Monthly	Discrete sample	Regression
Neill (1989)	River Burren, Ireland	Monthly	Discrete sample	Regression
Harned (1980)	Neuse R., NC, USA	Monthly to bi-monthly	Discrete sample	Flow-weighted Frequency
Dodd et al. (1992)	Neuse R., NC, USA	N/A	Point flow and export coefficients	Empirical model
NCDWQ (1999)	Neuse R., NC, USA	Monthly	Discrete sample	Trend analysis
Qian et al. (2000)	Neuse R., NC, USA	Monthly	Discrete sample	Seasonal trend
Stow et al. (2001)	Neuse R., NC, USA	Monthly	Discrete sample	Regression

Table 4. RiverNet depth-discharge relationships.

Site	Period	Discharge Equation $Q\ (m^3s^{-1})$	R^2	Discharge Range	Measured Range	% Coverage	Discharge Error %
NRCP	5/01-12/02	$Q=17.87(h)^{1.59}$	0.99	2 - 246 m^3s^{-1}	7 - 120 m^3s^{-1}	46%	$\pm$15
NRSS	1/01-12/02	$Q=23.30(h)^{1.42}$	0.99	7 - 207 m^3s^{-1}	11 - 184 m^3s^{-1}	87%	$\pm$17
NRB	1/01-12/02	$Q=8.85(h)^{2.31}$	0.98	5 - 294 m^3s^{-1}	8 - 178 m^3s^{-1}	59%	$\pm$15
CCH	9/01-12/02	$Q=2.34(h+0.24)^{2.53}$	0.99	1 - 94 m^3s^{-1}	2 - 56 m^3s^{-1}	58%	$\pm$11
CCG	1/01-12/02	$Q=0.95(h-1.17)^{3.31}$	0.99	2 - 93 m^3s^{-1}	2 - 71 m^3s^{-1}	76%	$\pm$15

Table 5. Annual discharge and water yield for sites in the Neuse River Basin. Data obtained from the USGS were used for sites FL, NRB, CCW, CCH, and BCL. ([a] *In 2001, NRCP monitored only from May to December*)

Station	**Annual Discharge (10^8 m^3 yr^{-1})** 2001	2002	**Water Yield (m)** 2001	2002
FL (USGS)	3.2 ± 0.3	3.5 ± 0.4	0.16 ± 0.02	0.18 ± 0.02
NRCP	2.2 ± 0.3[a]	7.3 ± 1.1	0.08 ± 0.01[a]	0.26 ± 0.04
NRSS	15 ± 2.6	15 ± 2.6	0.24 ± 0.04	0.24 ± 0.04
NRB (USGS)	22 ± 2.2	23 ± 2.3	0.22 ± 0.02	0.23 ± 0.02
CCW (USGS)	1.1 ± 0.1	1.2 ± 0.1	0.18 ± 0.02	0.20 ± 0.02
CCH (USGS)	4.7 ± 0.5	4.8 ± 0.5	0.25 ± 0.03	0.25 ± 0.03
CCG	5.8 ± 0.9	6.4 ± 1.0	0.23 ± 0.03	0.25 ± 0.04
BCL (USGS)	0.4 ± 0.1	0.4 ± 0.1	0.31 ± 0.05	0.29 ± 0.04
BCL (5/02-5/03)	0.4 ± 0.1		0.33 ± 0.05	

Table 6. Nitrate results at continuously monitored RiverNet stations.

Station	**Nitrate Load (10^5 kg N yr^{-1})** 2001	2002	**Nitrate Yield (kg N km^{-2})** 2001	2002	**Mean Nitrate Concentration (mg N L^{-1})** 2001	2002
NRCP	1.5 ± 0.2[a]	3.7 ± 0.6	53 ± 8.0[a]	130 ± 21	0.67 ± 0.11	0.50 ± 0.08
NRSS	6.2 ± 1.1	6.4 ± 1.2	96 ± 18	99 ± 18	0.41 ± 0.08	0.42 ± 0.08
NRB	11 ± 1.0	11 ± 1.0	100 ± 13	110 ± 13	0.48 ± 0.06	0.48 ± 0.06
CCH	0.3 ± 0.03[b]	2.2 ± 0.3	16 ± 2.0[b]	120 ± 13	0.62 ± 0.07	0.46 ± 0.06
CCG	2.8 ± 0.5	2.9 ± 0.5	110 ± 18	120 ± 19	0.49 ± 0.08	0.46 ± 0.08
BCL (5/02 – 5/03)	1.0 ± 0.2		820 ± 120		2.50 ± 0.38	

Table 7. Mass balance for annual nitrate and discharge in three reaches of the Neuse River Basin during 2002.

Reach (station #s)	**Reach Length** (km)	**Δ NO_3^- Load** (10^5 kg N)	**Δ Discharge** (10^8 m^3)	**Mean NO_3^- Concentration of Discharge Added in Reach** (mg N L^{-1})
NRCP – NRSS (4 – 10)	151.7	2.7 $\pm$ 1.8	7.9 $\pm$ 3.7	0.34
NRSS – NRB (10 – 12)	76.0	4.8 $\pm$ 2.5	7.8 $\pm$ 6.0	0.61
CCH – CCG (20 – 21)	26.0	0.70 $\pm$ 0.75	1.5 $\pm$ 1.4	0.45

Table 8. Dissolved nitrogen speciation in Neuse River Basin from 2001-02 discrete water samples. BCL includes 2003 samples during the continuous monitoring period at that location.

Station #	Station Name	N	DIN (mg N L^{-1}) NO_3^-	NH_4^+	DON	TDN	% DIN
1	FL	23	0.09 ± 0.08	0.10 ± 0.08	0.66 ± 0.22	0.85 ± 0.19	23 ± 21
2	NR1	23	0.17 ± 0.09	0.10 ± 0.07	0.56 ± 0.22	0.83 ± 0.24	33 ± 17
3	NRP	26	0.29 ± 0.10	0.07 ± 0.06	0.58 ± 0.20	0.94 ± 0.20	40 ± 15
4	NRCP	48	0.54 ± 0.17	0.07 ± 0.05	0.61 ± 0.29	1.22 ± 0.33	52 ± 15
5	NRC-42	25	0.89 ± 0.32	0.06 ± 0.05	0.67 ± 0.21	1.62 ± 0.36	58 ± 12
6	NRS-70	23	0.76 ± 0.24	0.05 ± 0.04	0.60 ± 0.19	1.41 ±0.35	57 ± 10
7	NRS-301	16	0.69 ± 0.17	0.09 ± 0.12	0.57 ± 0.24	1.35 ± 0.28	59 ± 15
8	NRS-1201	41	0.48 ± 0.16	0.05 ± 0.06	0.54 ± 0.23	1.07 ± 0.27	52 ± 17
9	NRG	24	0.53 ± 0.10	0.04 ± 0.03	0.68 ± 0.14	1.25 ± 0.16	46 ± 8
10	NRSS	40	0.49 ± 0.14	0.05 ± 0.05	0.64 ± 0.22	1.18 ± 0.28	48 ± 17
11	NRK	21	0.55 ± 0.15	0.04 ± 0.03	0.61 ± 0.14	1.20 ± 0.21	49 ± 9
12	NRB	46	0.50 ± 0.18	0.04 ± 0.03	0.73 ± 0.16	1.27 ± 0.25	42 ± 11
13	SCC	19	0.21 ± 0.09	0.05 ± 0.03	0.64 ± 0.18	0.90 ± 0.23	29 ± 8
14	SCS	21	0.20 ± 0.16	0.04 ± 0.07	0.56 ± 0.29	0.80 ± 0.34	30 ± 18
15	MCC	20	0.58 ± 0.20	0.07 ± 0.07	0.72 ± 0.21	1.37 ± 0.27	48 ± 11
16	MCS	21	0.35 ± 0.13	0.04 ± 0.04	0.66 ± 0.21	1.05 ± 0.23	38 ± 14
17	BCS	21	0.08 ± 0.05	0.06 ± 0.07	0.74 ± 0.24	0.88 ± 0.27	17 ± 9
18	LRG	21	0.24 ± 0.13	0.03 ± 0.03	0.74 ± 0.27	1.01 ± 0.31	28 ± 13
19	CCW	19	0.10 ± 0.11	0.02 ± 0.02	0.74 ± 0.26	0.86 ± 0.25	13 ± 12
20	CCH	38	0.53 ± 0.16	0.07 ± 0.05	0.82 ± 0.34	1.42 ± 0.40	43 ± 10
21	CCG	44	0.50 ± 0.15	0.07 ± 0.06	0.71 ± 0.21	1.28 ± 0.27	44 ± 11
22	BCL	43	2.32 ± 0.60	0.17 ± 0.27	0.53 ± 0.29	3.02 ± 0.81	82 ± 8

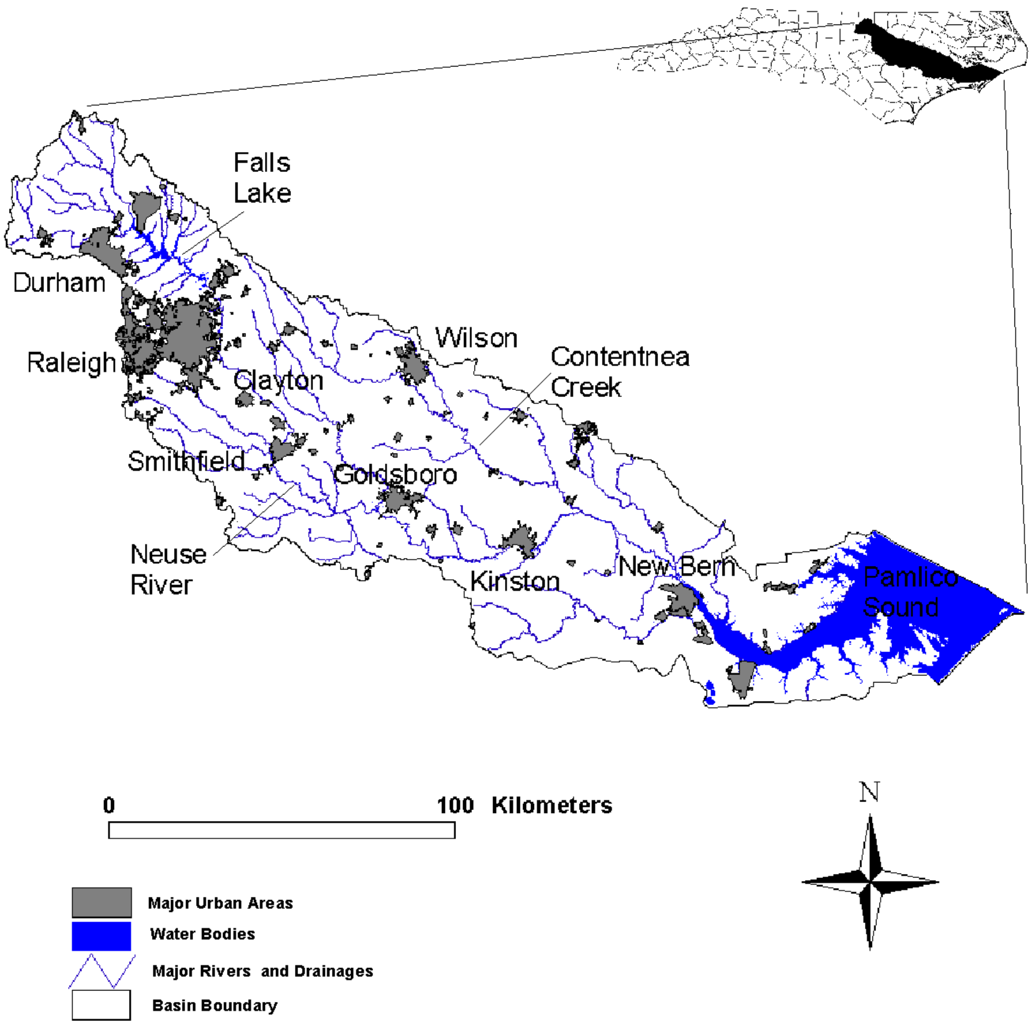


Figure 1. Neuse River Basin, North Carolina.

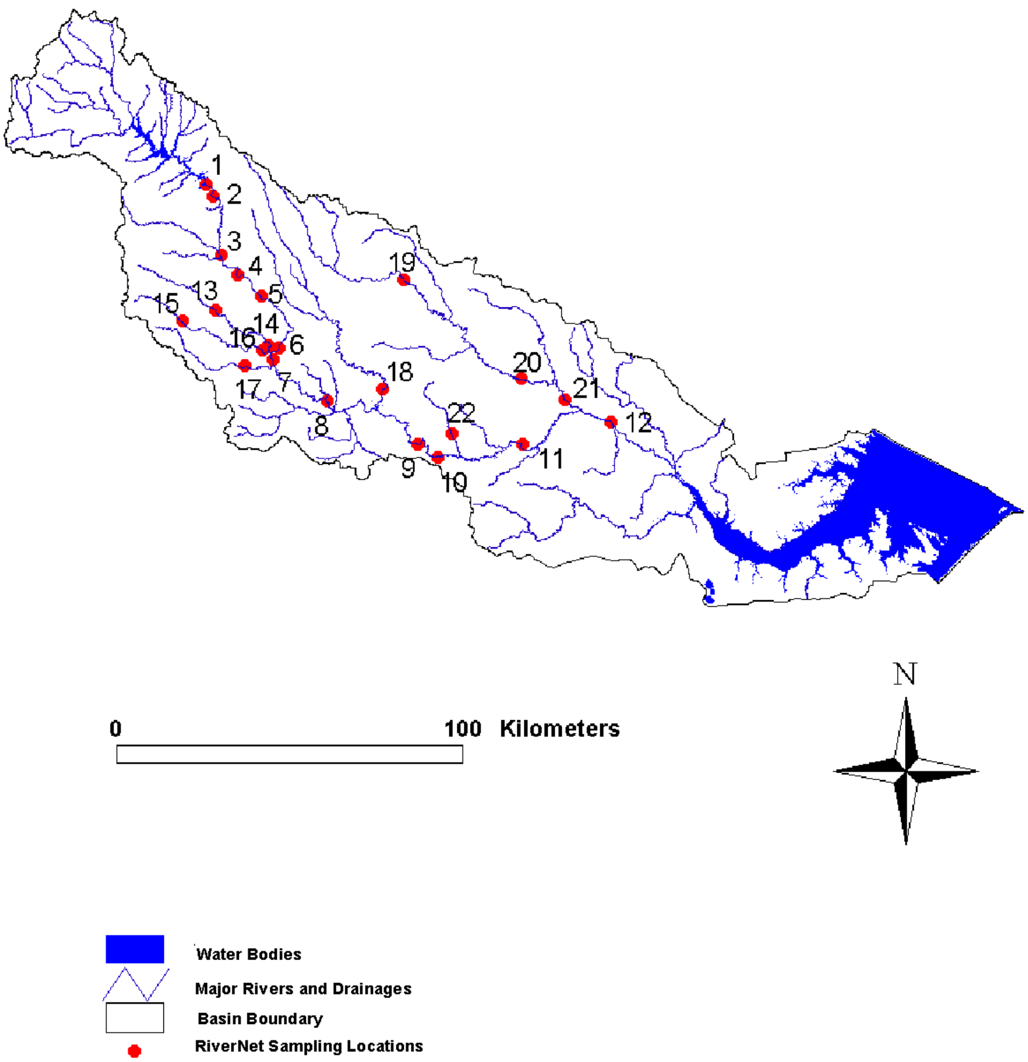
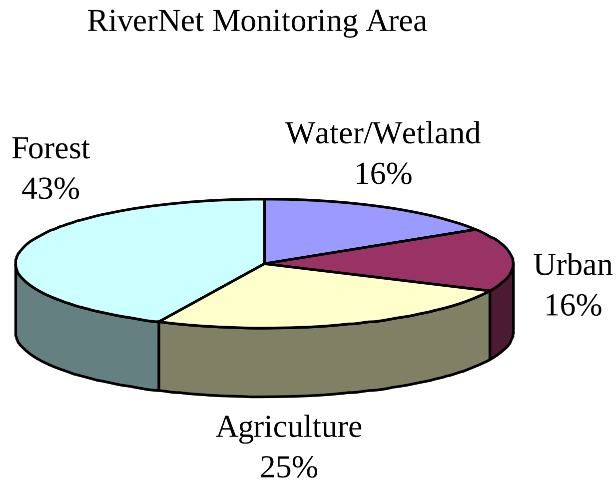


Figure 2. RiverNet monitoring locations 2001-02.



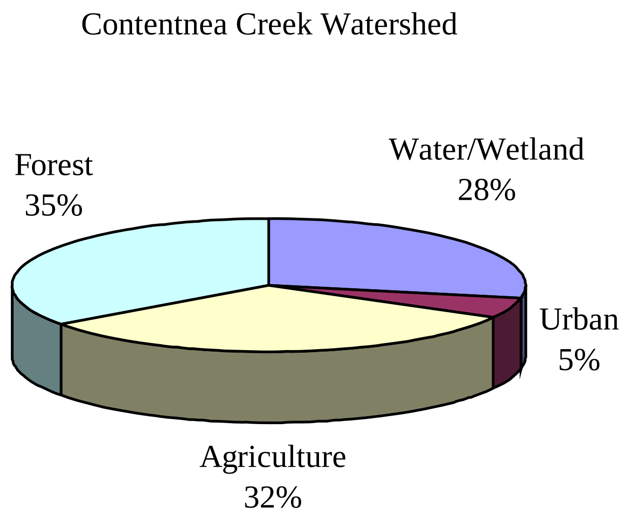
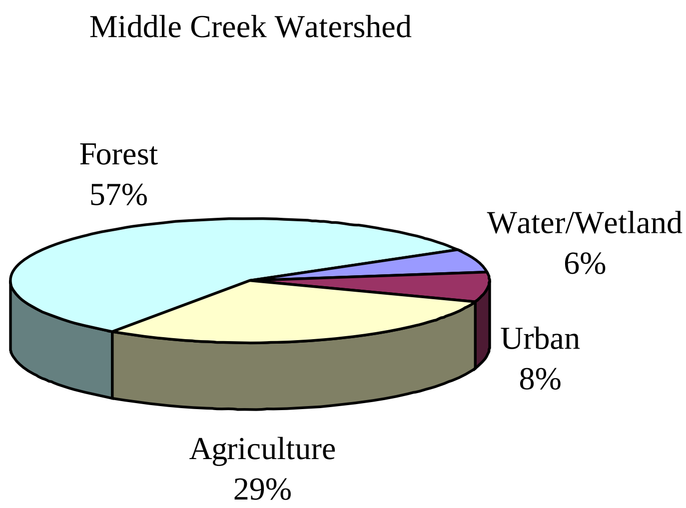


Figure 3. Land use in the RiverNet monitoring area and Contentnea Creek subbasin. The RiverNet monitoring area encompasses the Contentnea Creek subbasin.



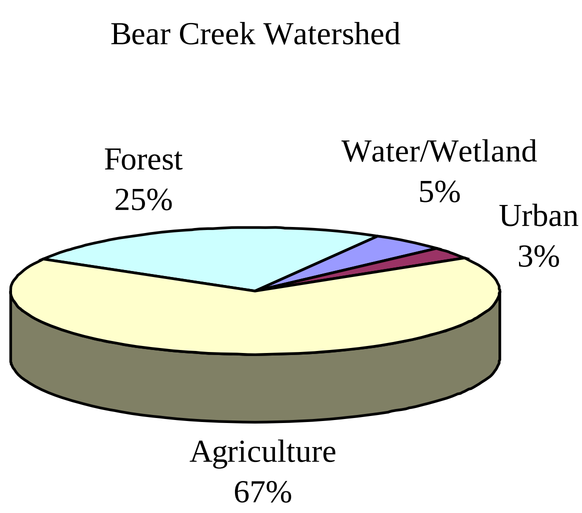


Figure 4. Land use in Middle and Bear Creeks.

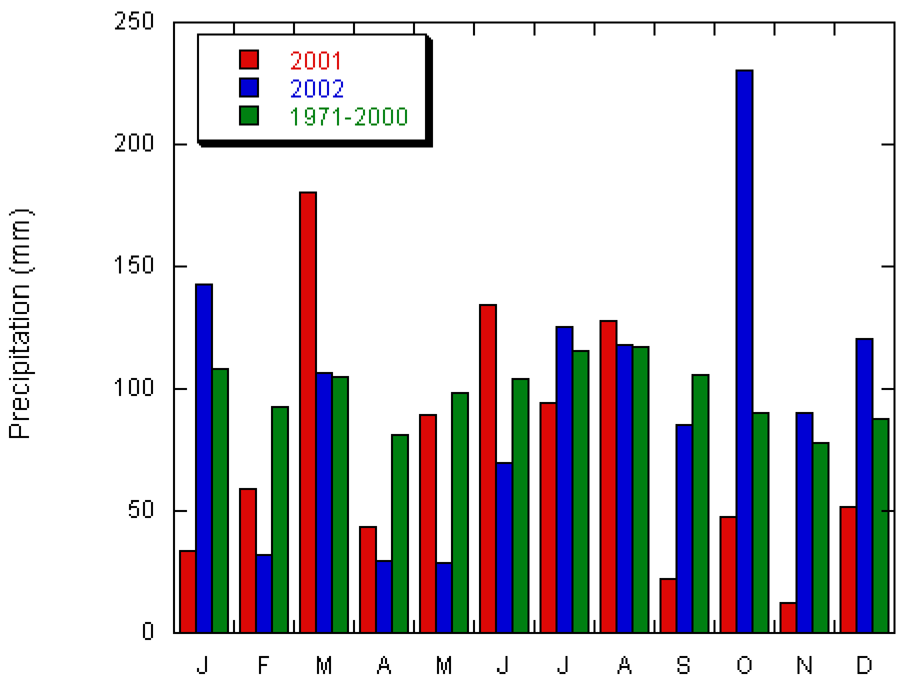


Figure 5. Monthly precipitation in the Neuse River Basin 2001-02 versus longterm average. Precipitation measured at the Raleigh-Durham Airport in the Upper Neuse Basin (State Climate Office, 2003; NOAA, 2004).

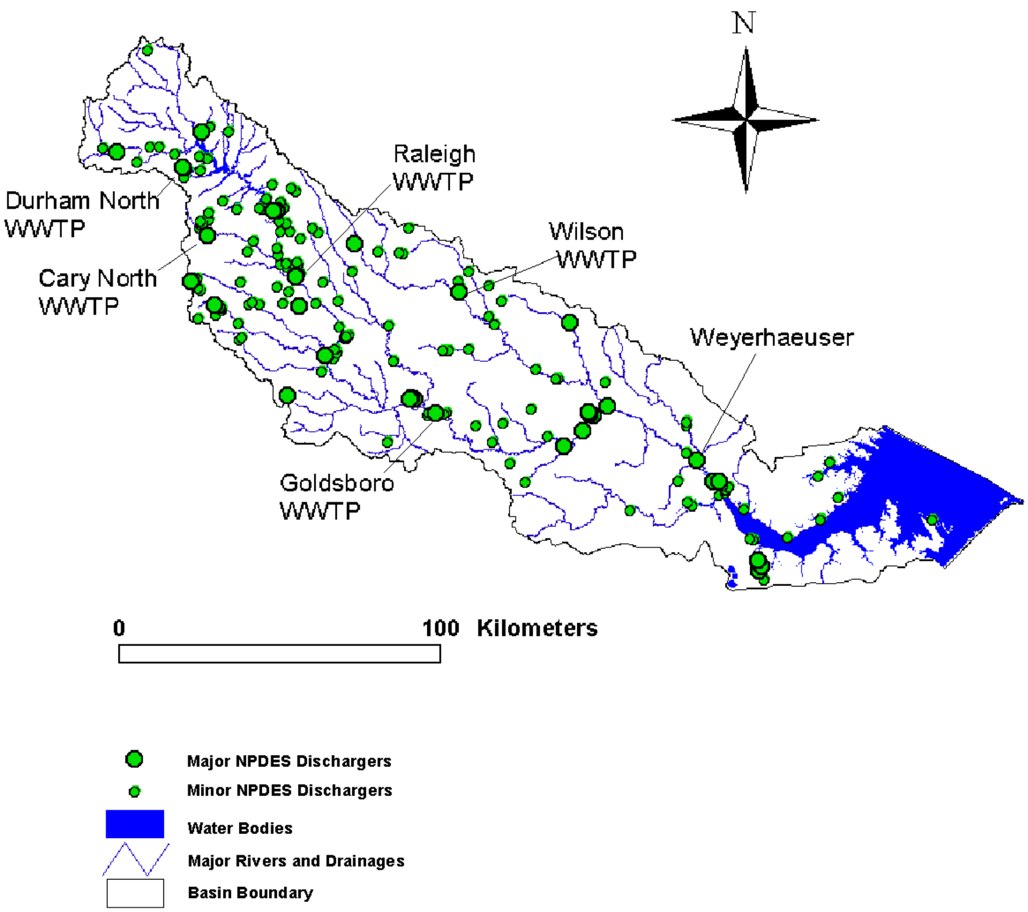


Figure 6. Nitrogen point sources (NPDES). Major NPDES facilities are permitted for $\geq 3.8 \times 10^3\ m^3 day^{-1}$. Those labeled are permitted for $\geq 3.8 \times 10^4 m^3 day^{-1}$.

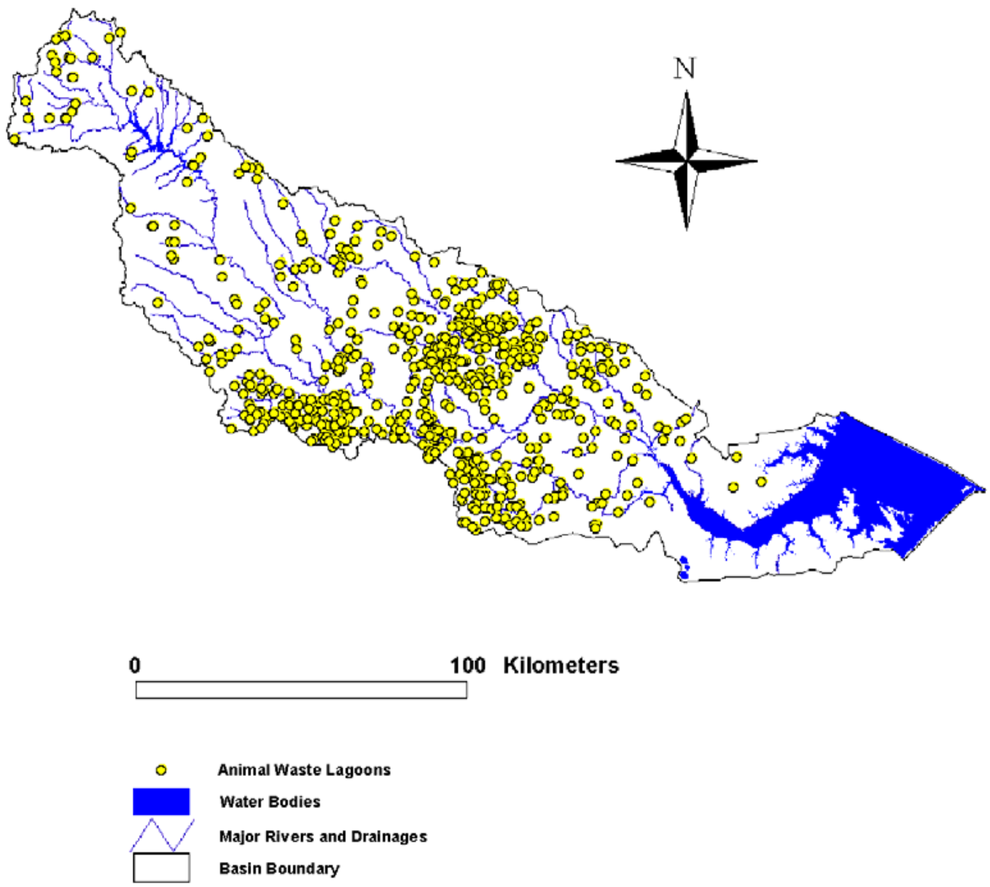


Figure 7. Nitrogen nonpoint sources (CAFOs).

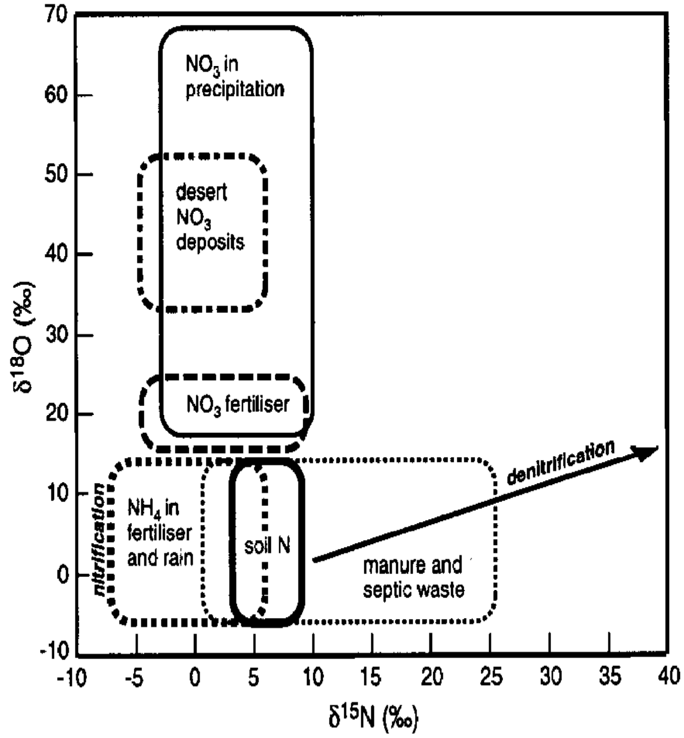


Figure 8. Stable isotopic variation of oxygen and nitrogen in various nitrogen sources. From Kendall 1998.

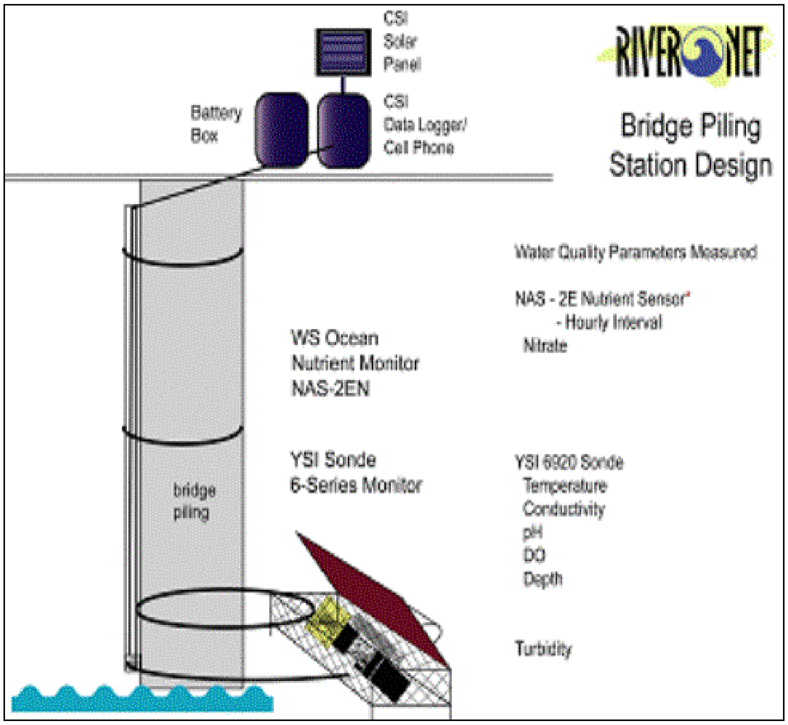


Figure 9. RiverNet monitoring station.

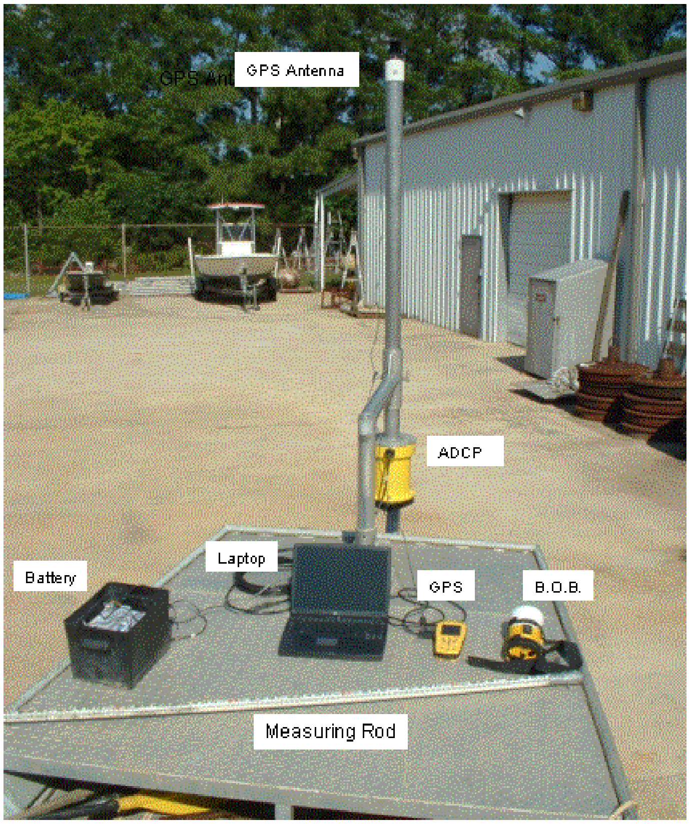
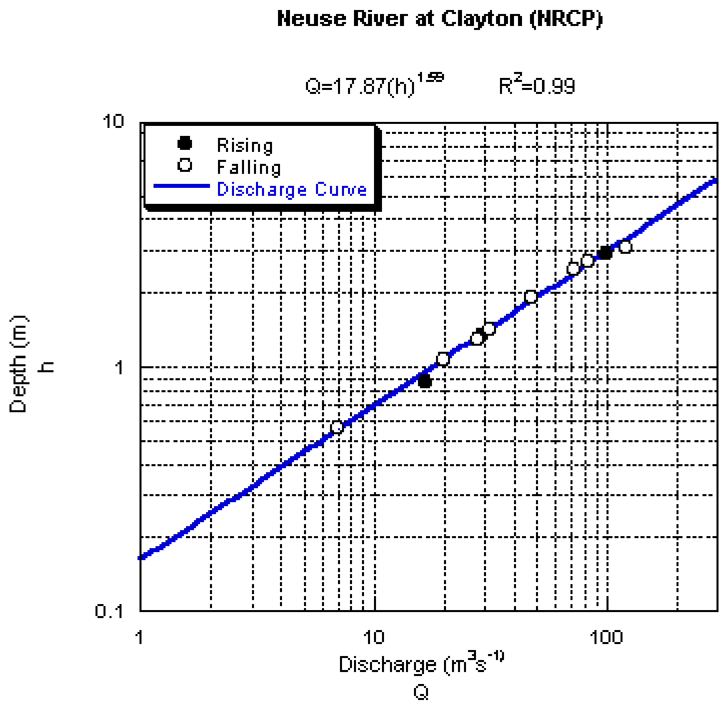


Figure 10. Acoustic Doppler Current profiler (ADCP) setup. GPS tracking and real-time differential correction using the Trimble Beacon-on-belt (B.O.B) was used during flow periods when bottom tracking was insufficient.



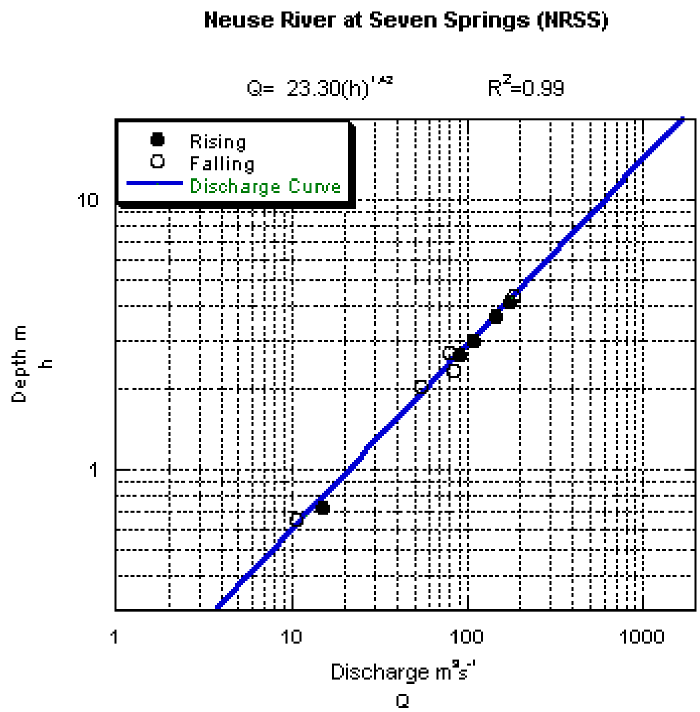


Figure 11. Upper Neuse River mainstem depth-discharge relationships.

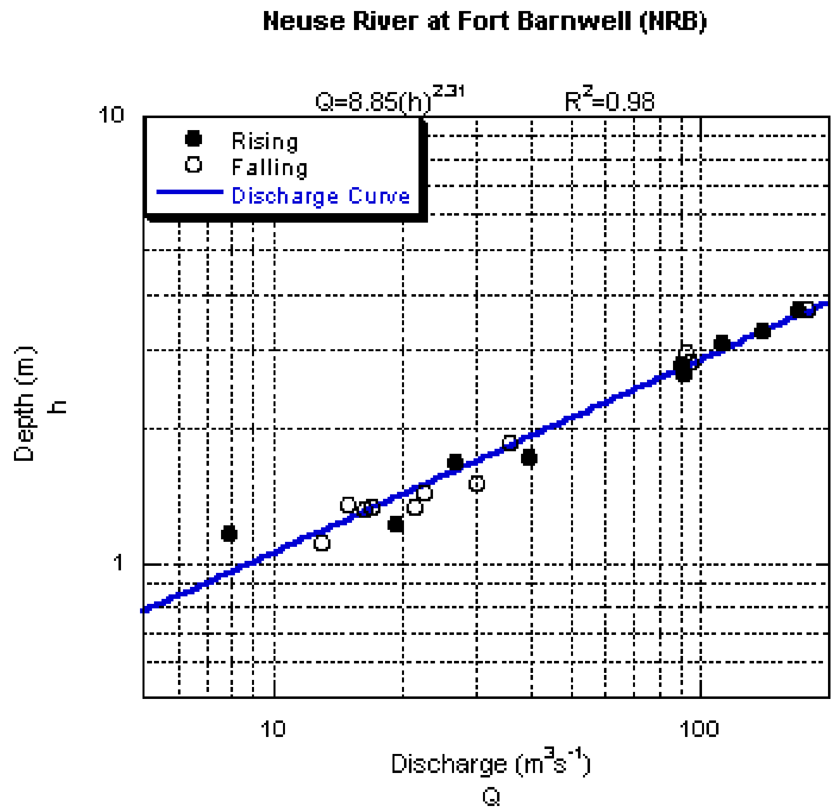


Figure 12. Lower Neuse River mainstem stage-discharge relationship. Note: nine discrete discharge measurements made by USGS personnel below overflow conditions (<104 m^3s^{-1}) were added to better clarify the center of the measured range (USGS, 2003).

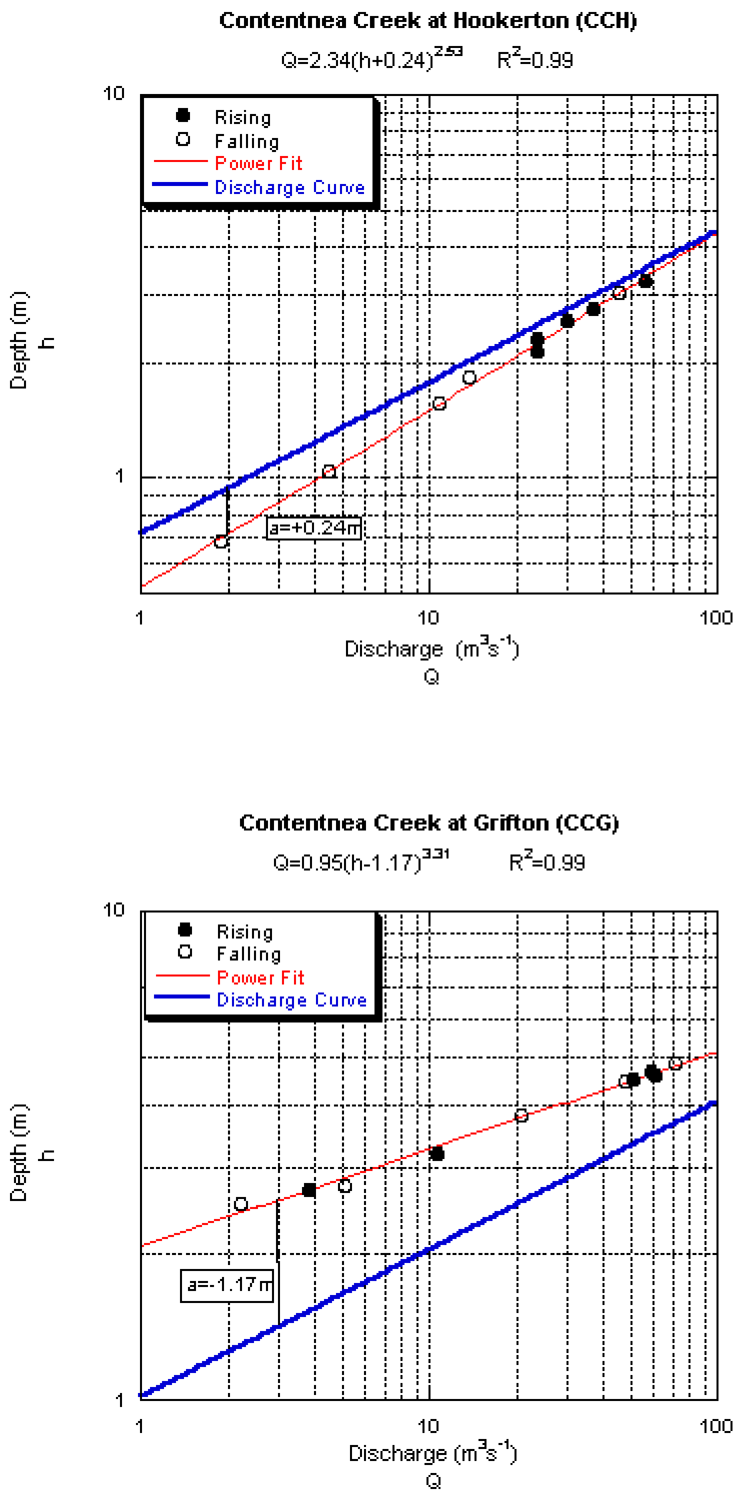


Figure 13. Contentnea Creek depth-discharge relationships.

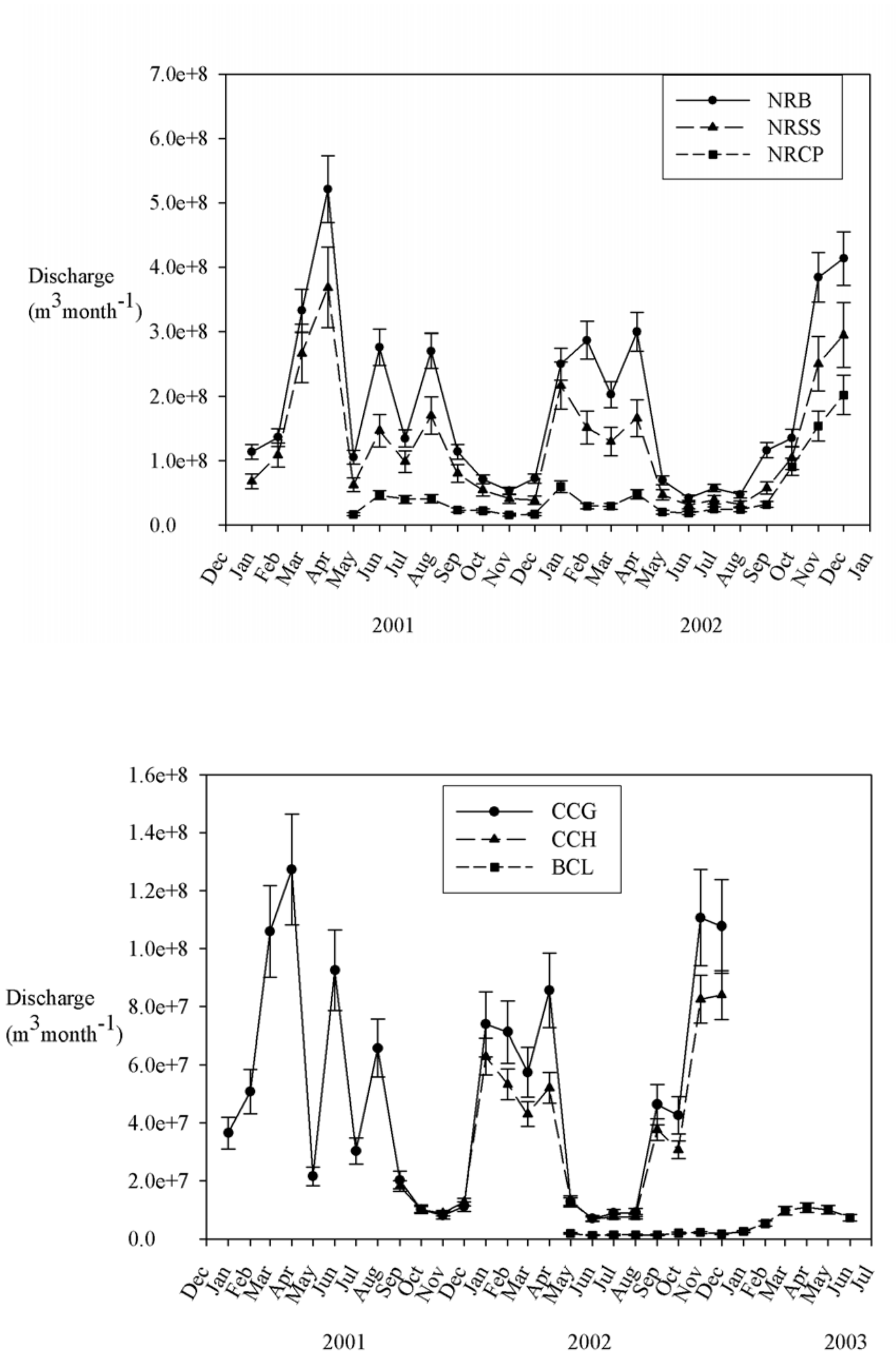
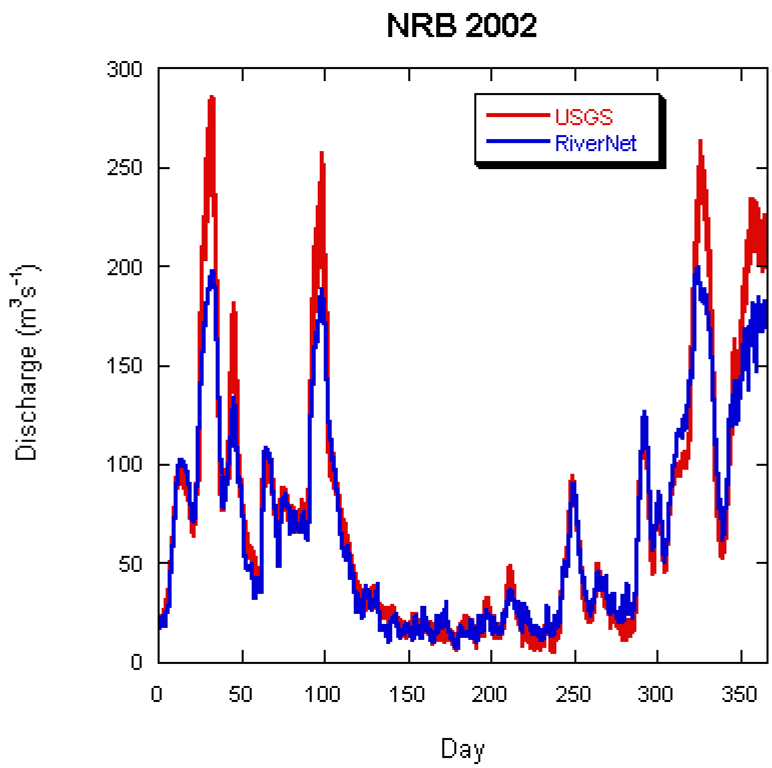


Figure 14. Monthly discharge at RiverNet monitoring sites.



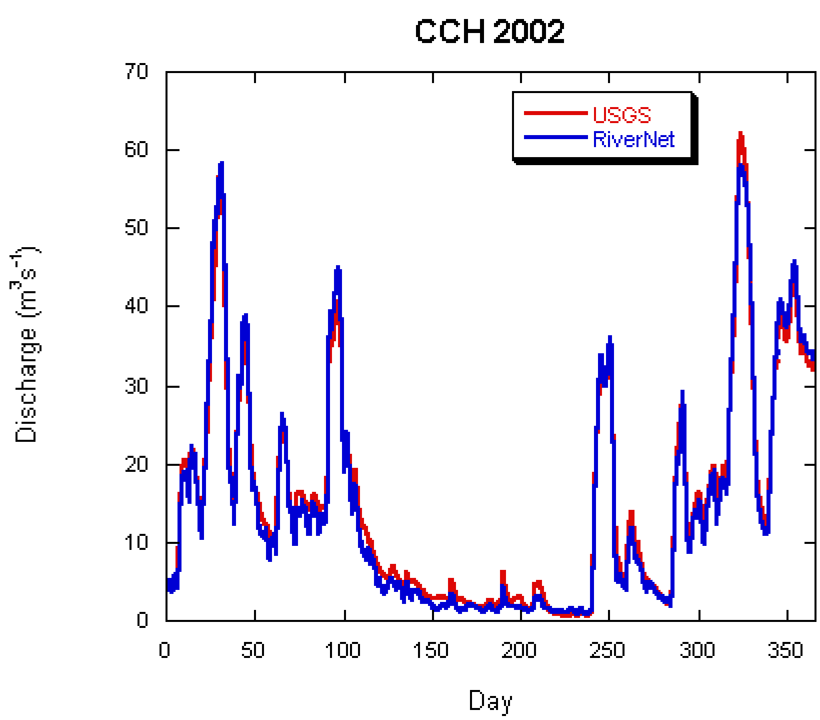
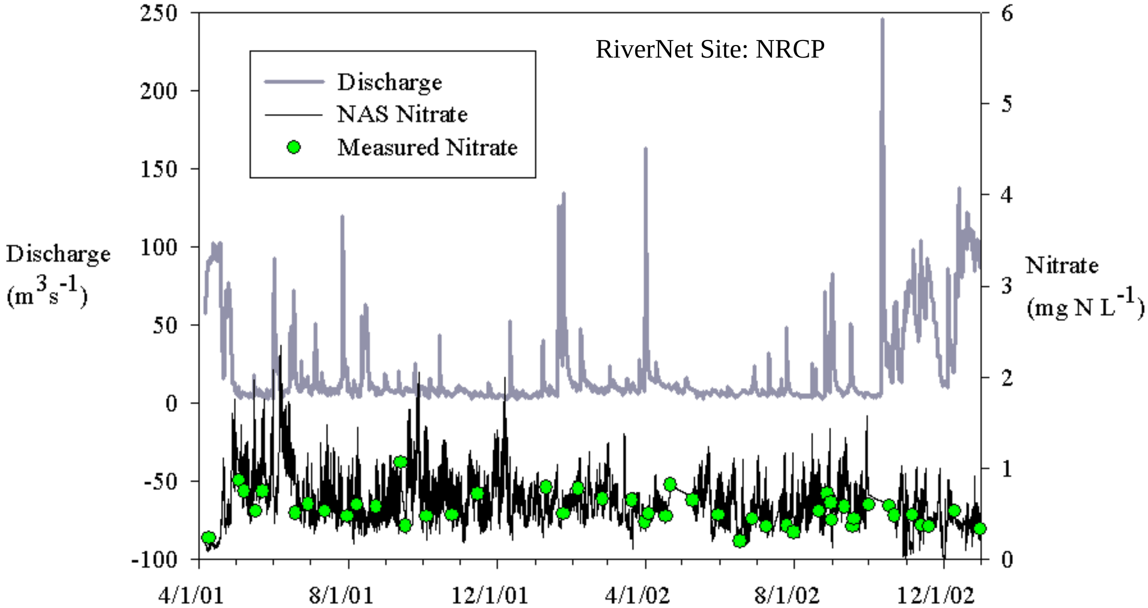


Figure 15. Comparison of discharge between USGS and RiverNet. Co-located sites at Fort Barnwell (NRB) and Hookerton (CCH). Overflow conditions were present at flows greater than 104-116 m^3s^{-1} at NRB.



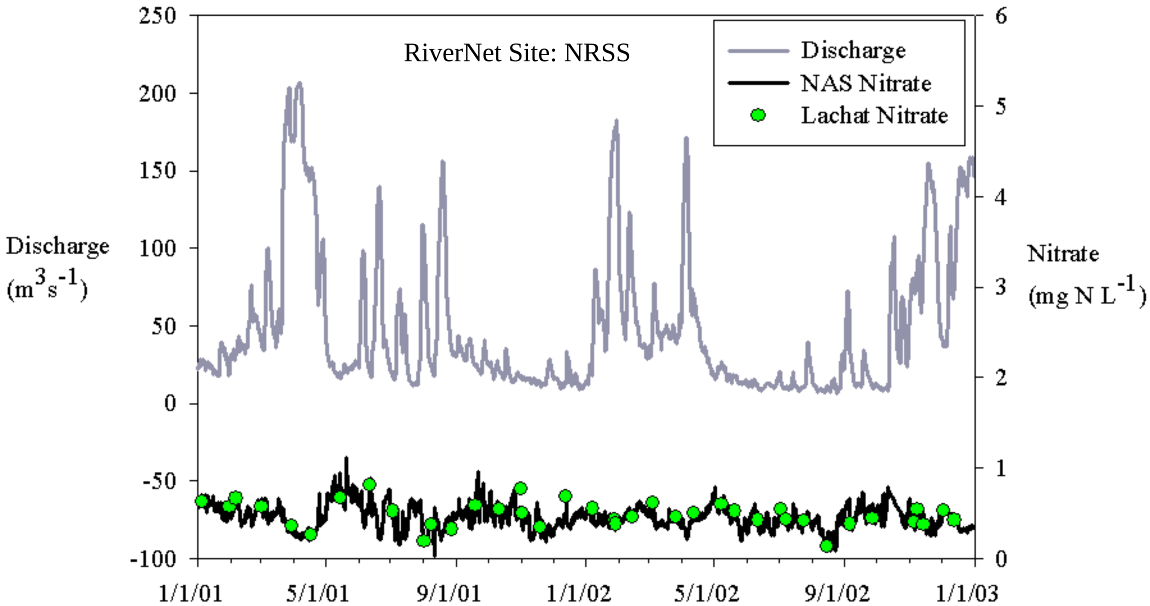
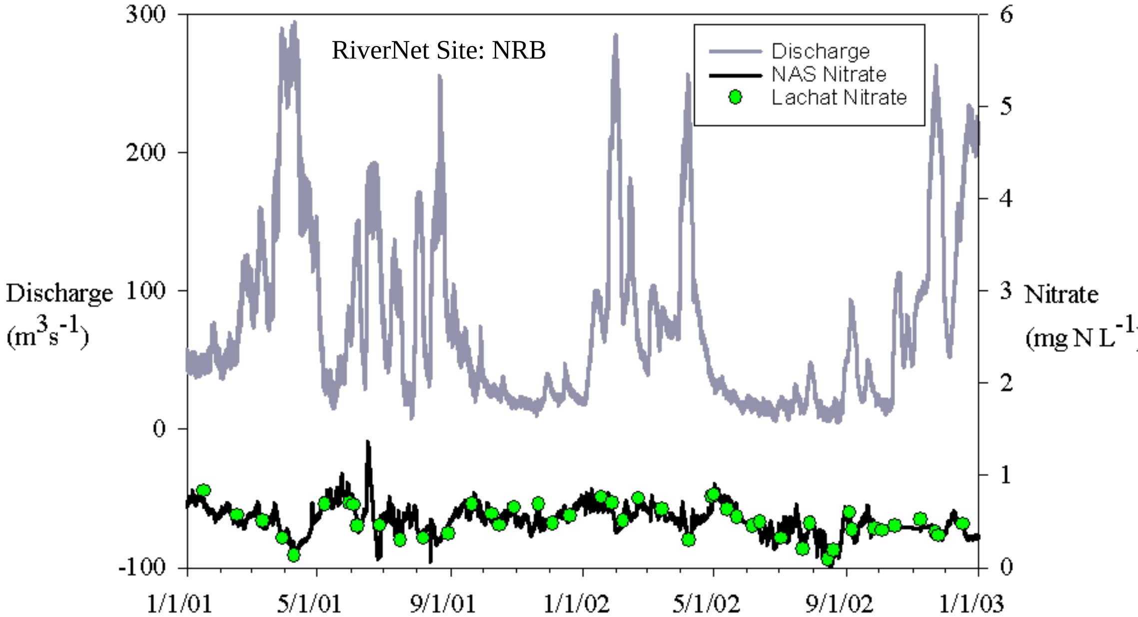


Figure 16. Upper Neuse River nitrate concentration variability.



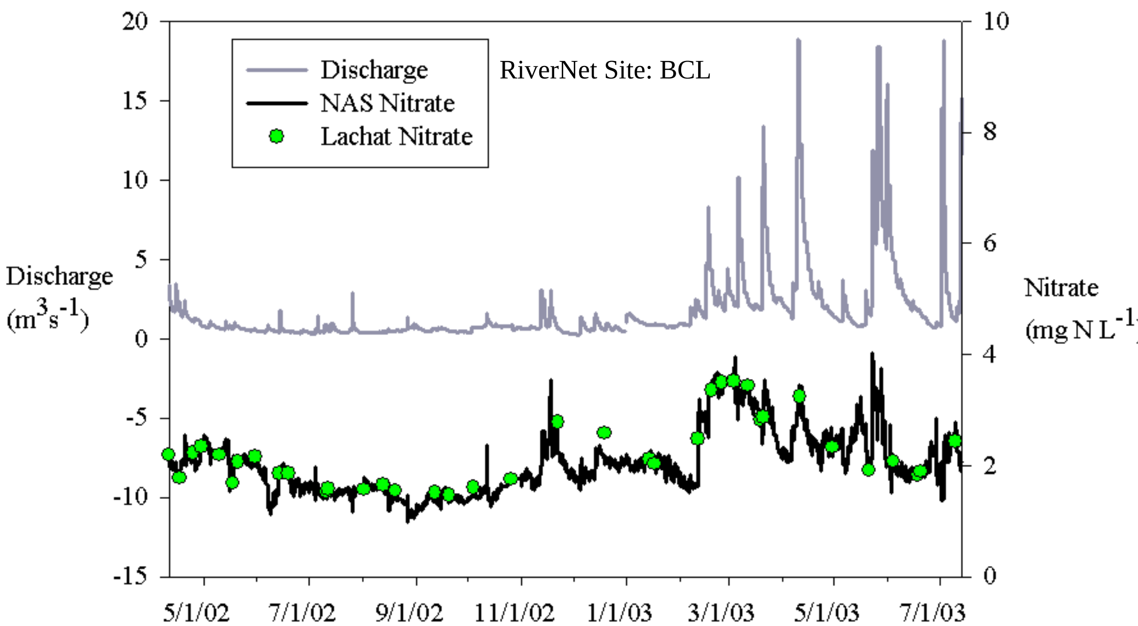


Figure 17. Lower Neuse River and Bear Creek nitrate concentration variability.

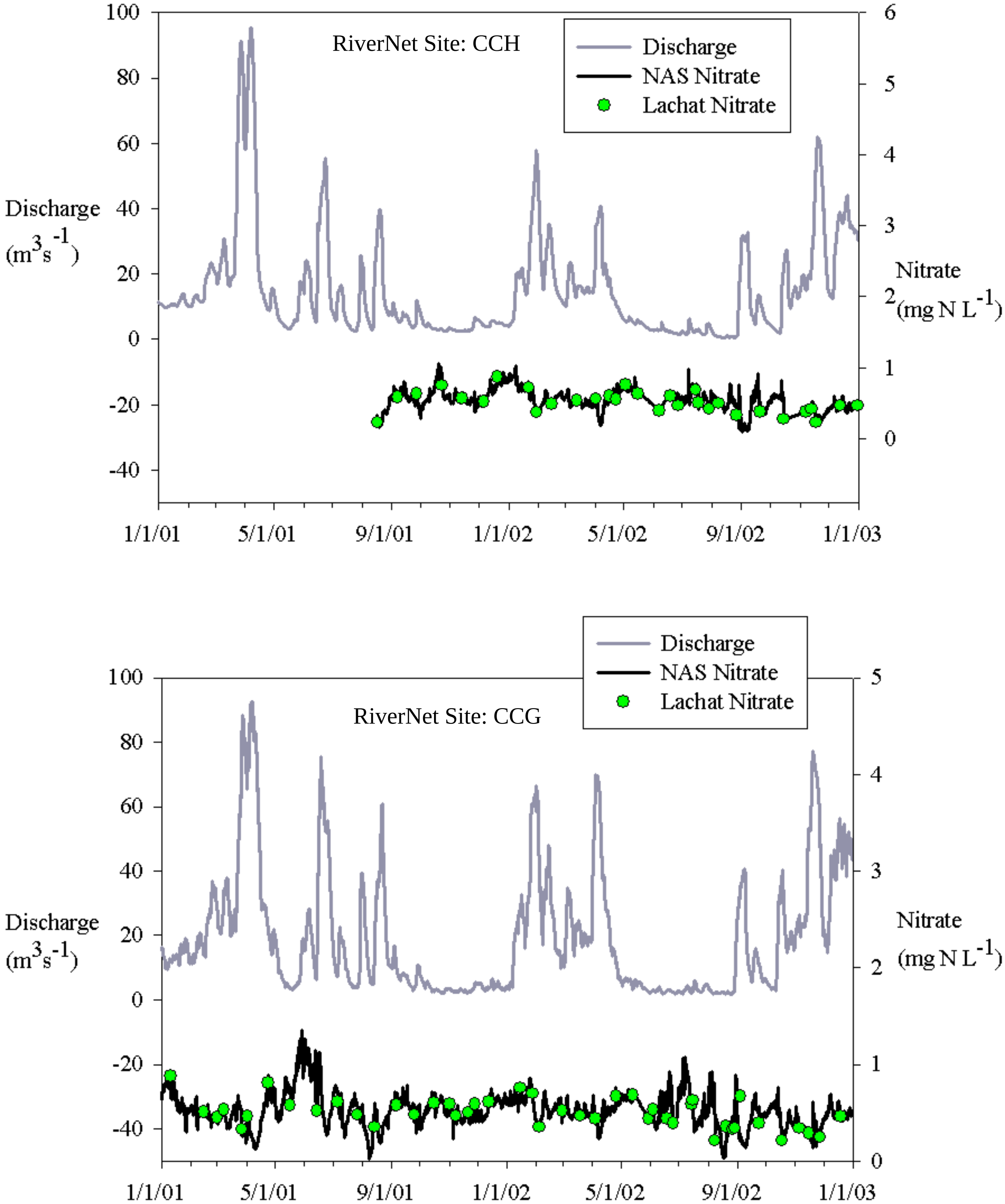


Figure 18. Contentnea Creek nitrate concentration variability.

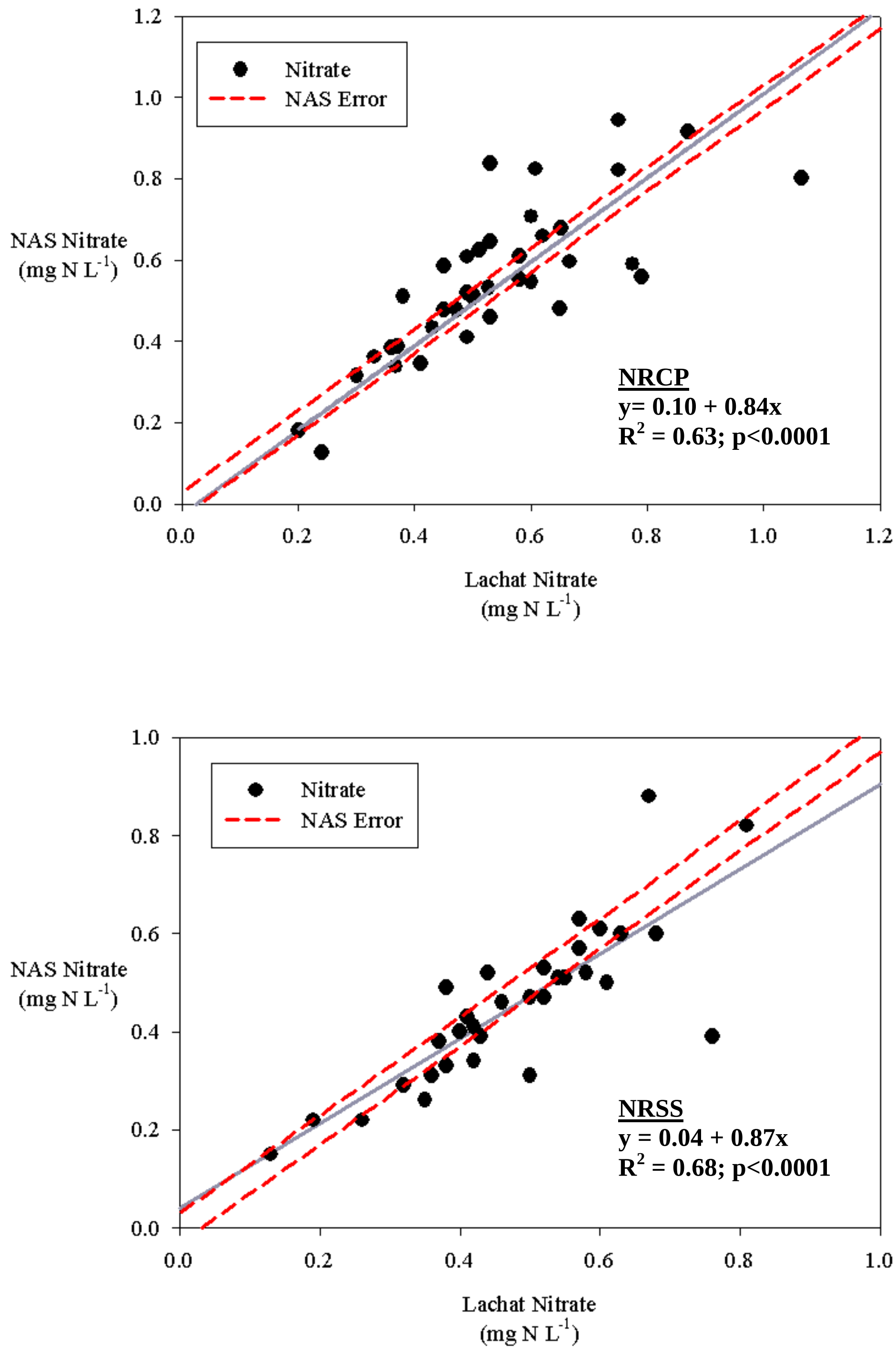


Figure 19. Continuous monitoring of nitrate (NAS) versus discreet sampling (Lachat) in the Upper Neuse River 2001-02. The NAS error limits are $\pm$ 0.03 mg N L^{-1} about a 1-1 regression line.

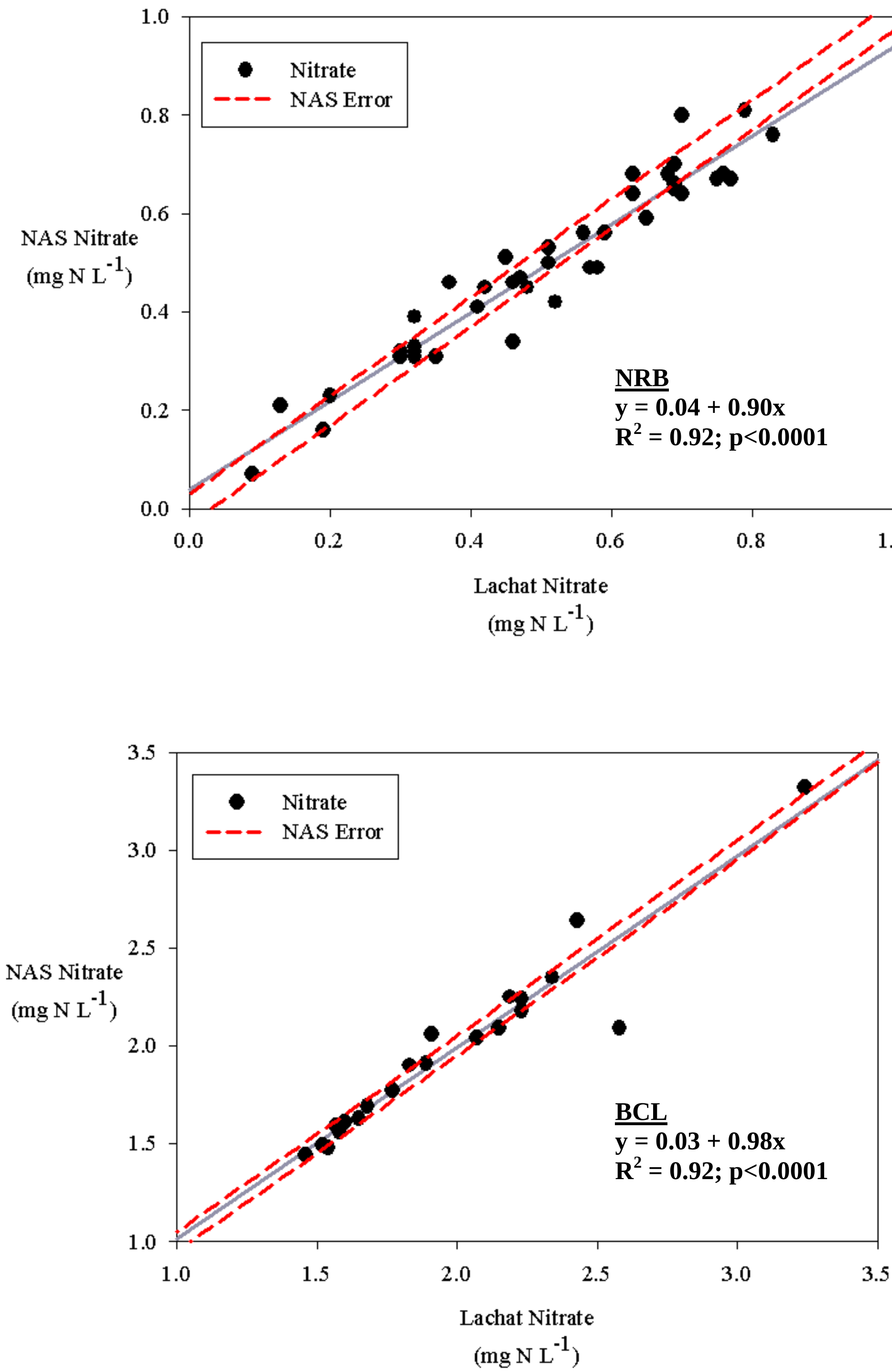
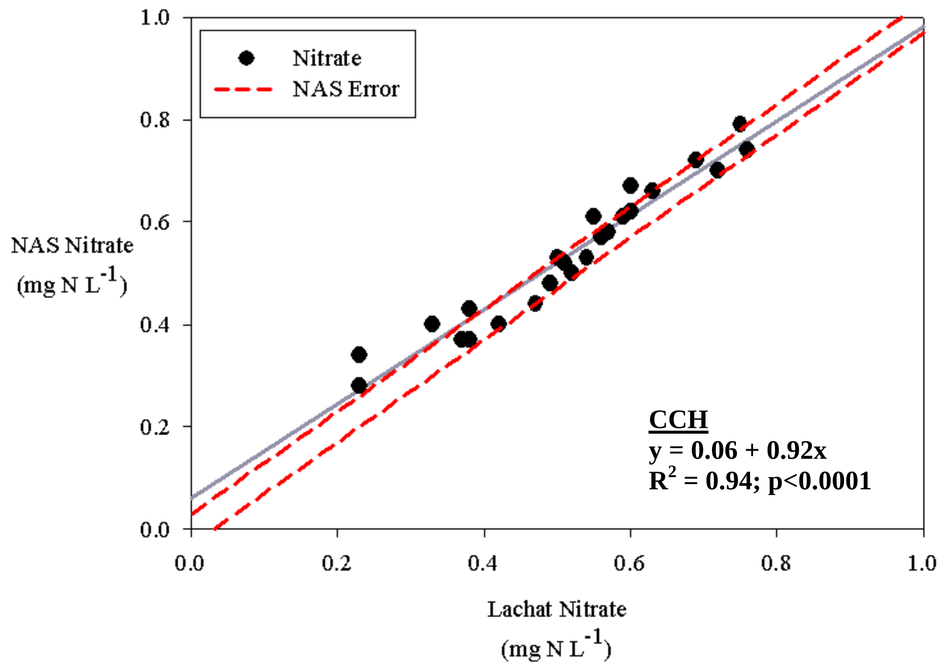


Figure 20. Continuous monitoring of nitrate versus discrete sampling in the Lower Neuse River and Bear Creek 2001-02. NAS error limits are defined as $\pm$ 0.03 mg N L^{-1} for NRB and $\pm$ 0.05 mg N L^{-1} for BCL.



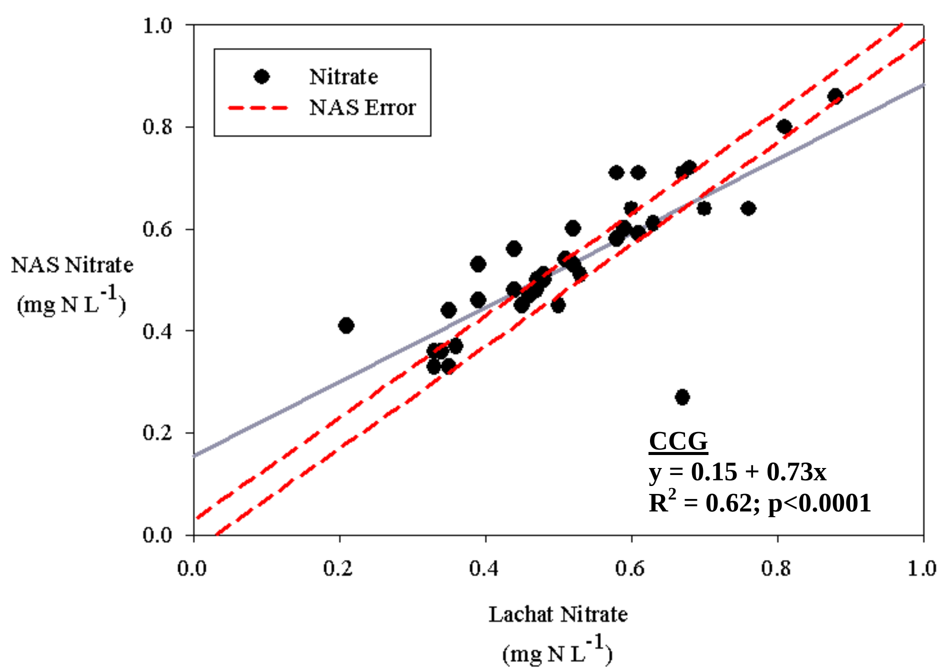


Figure 21. Continuous monitoring of nitrate versus discrete sampling in Contentnea Creek 2001-02. NAS error is defined at $\pm$ 0.03 mg N L^{-1}.

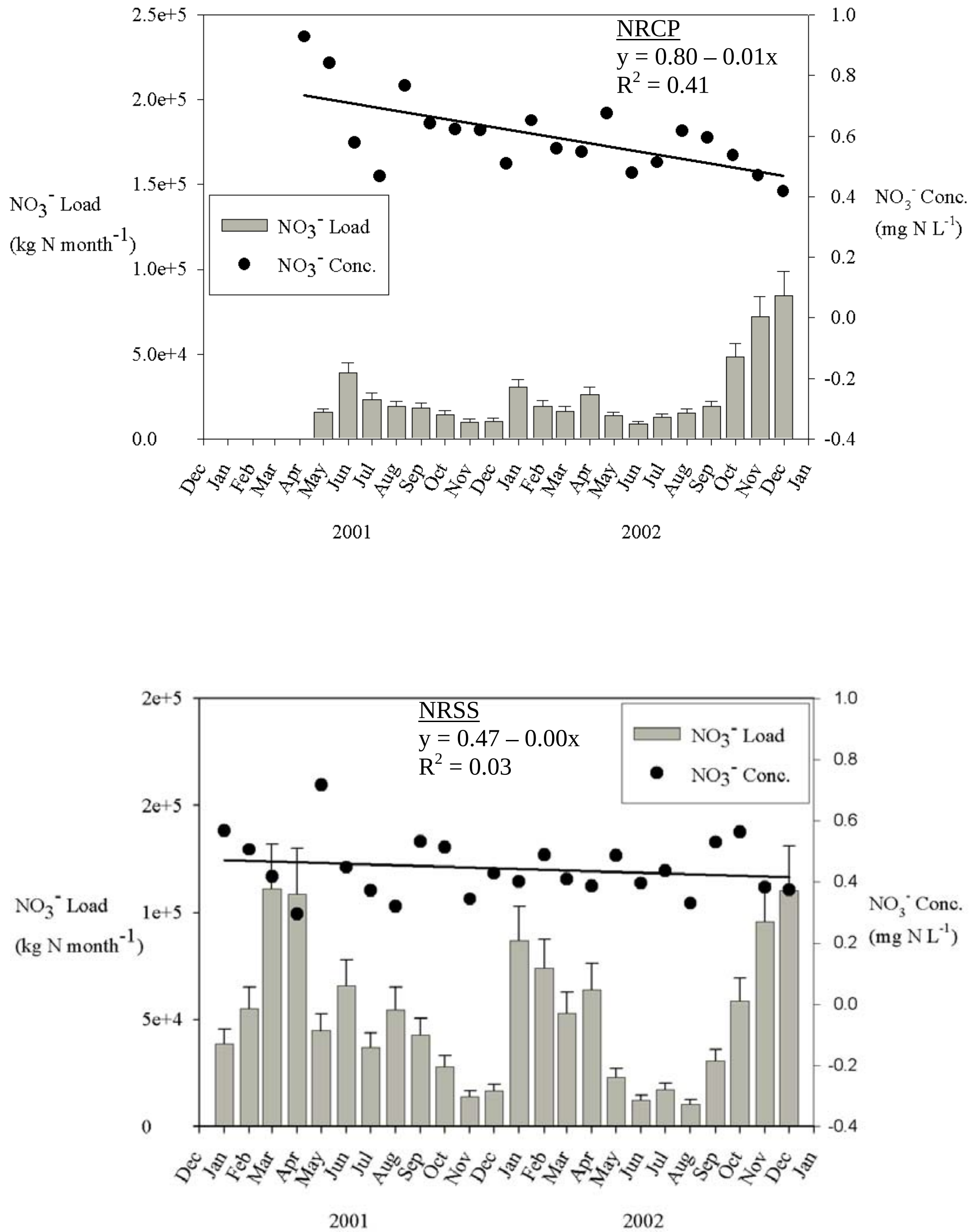
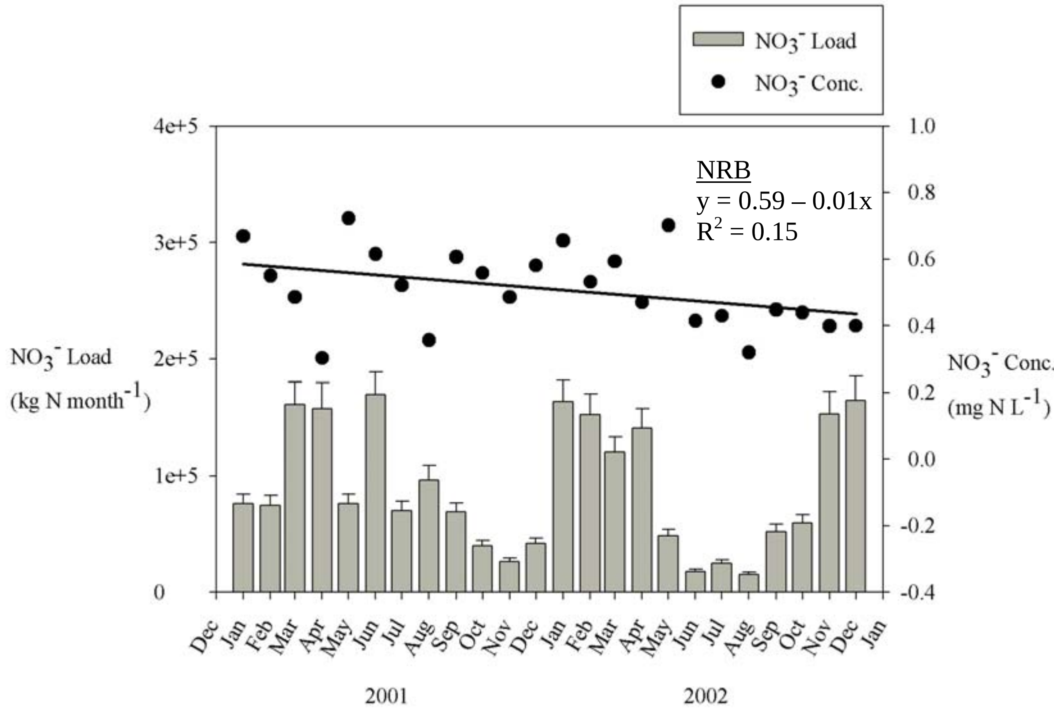


Figure 22. Monthly nitrate loads and flow-normalized nitrate concentrations in the Upper Neuse River.



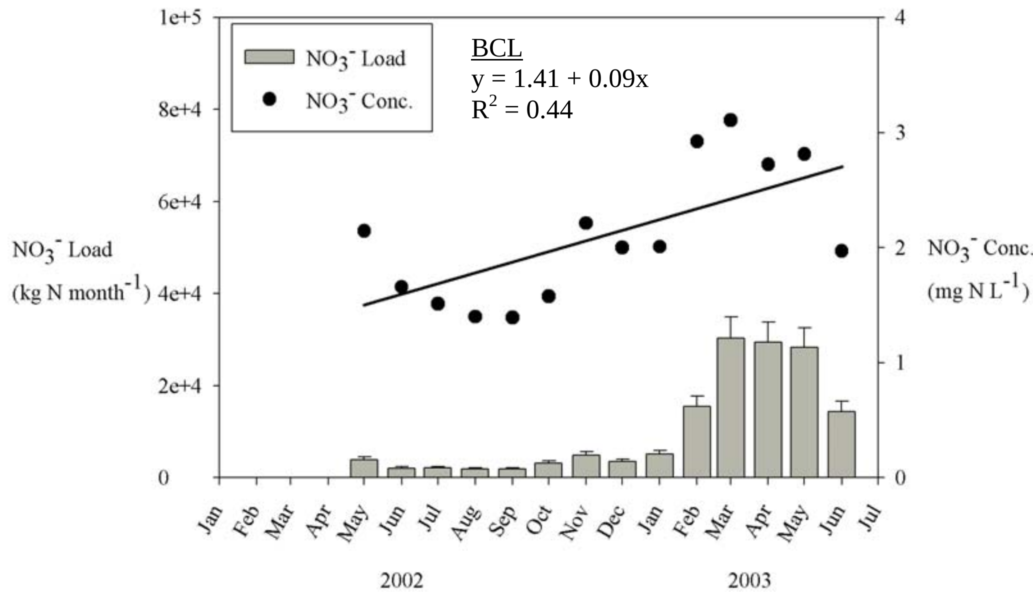
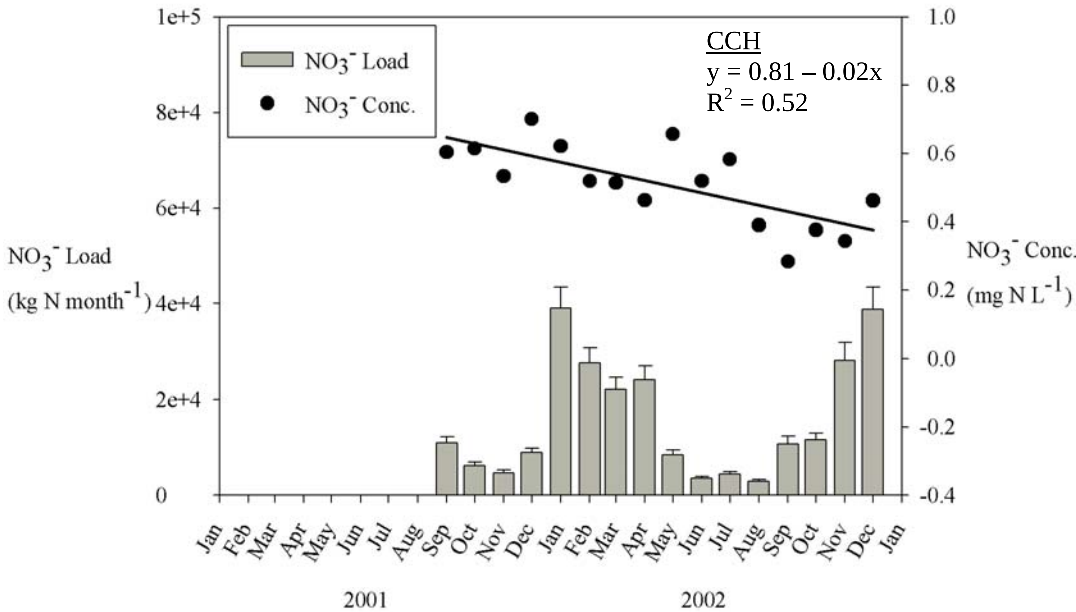


Figure 23. Monthly nitrate loads and flow-normalized nitrate concentrations in the Lower Neuse River and Bear Creek.



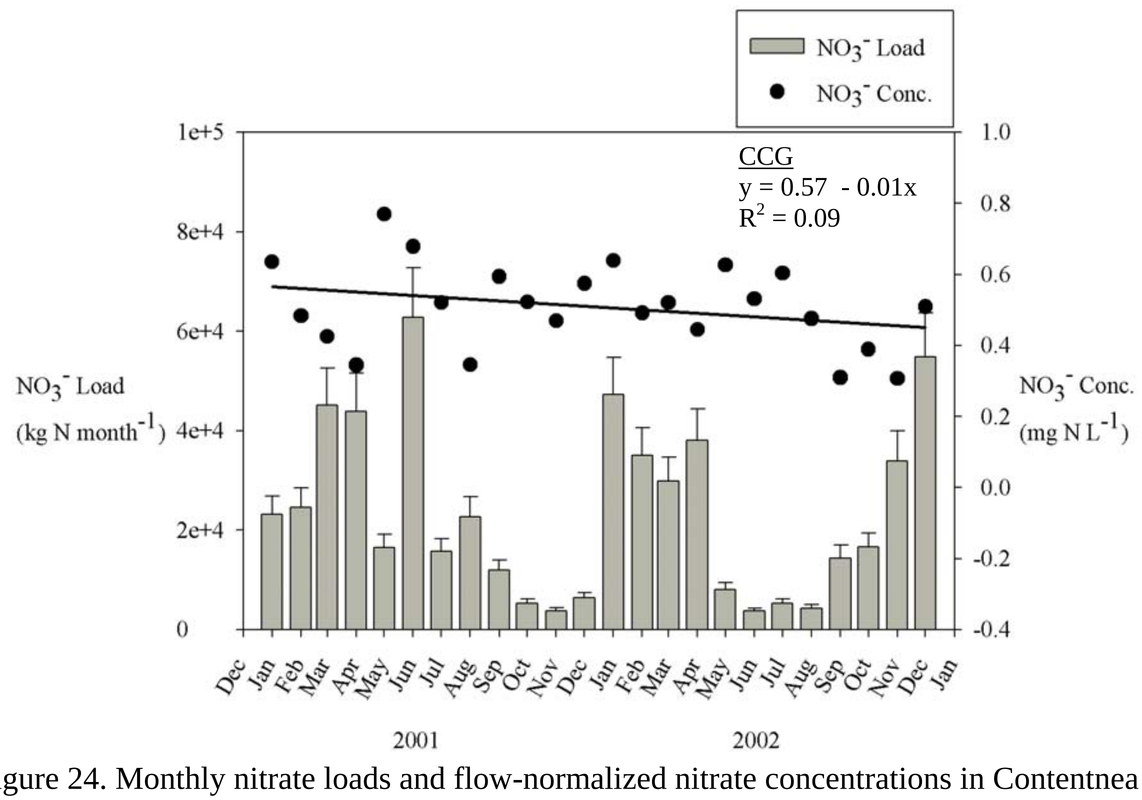
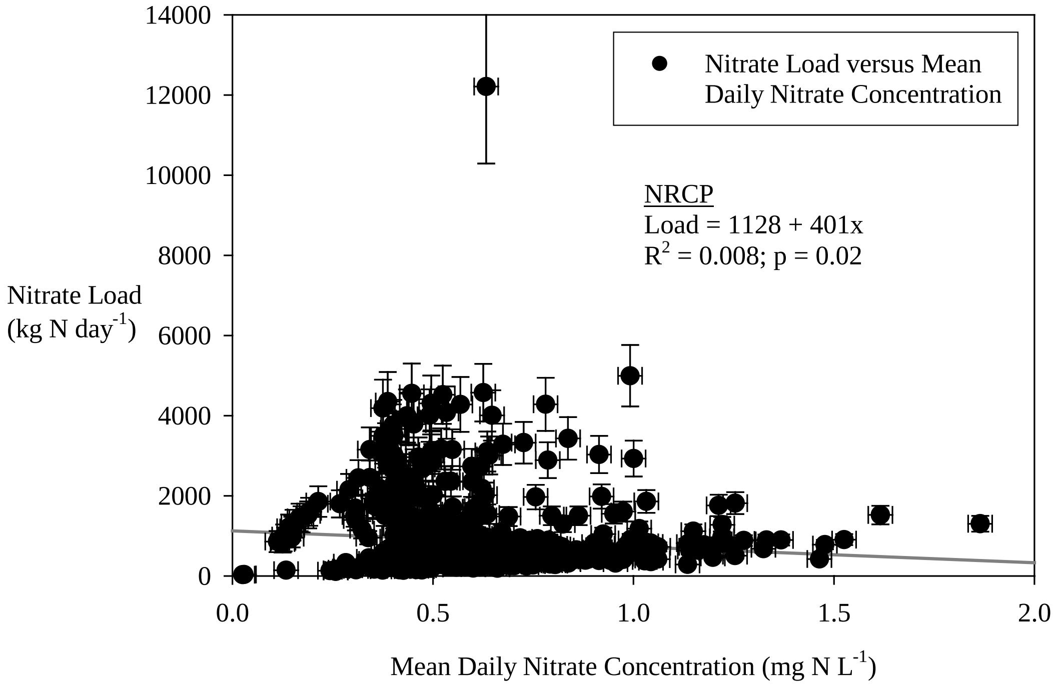


Figure 24. Monthly nitrate loads and flow-normalized nitrate concentrations in Contentnea Creek.



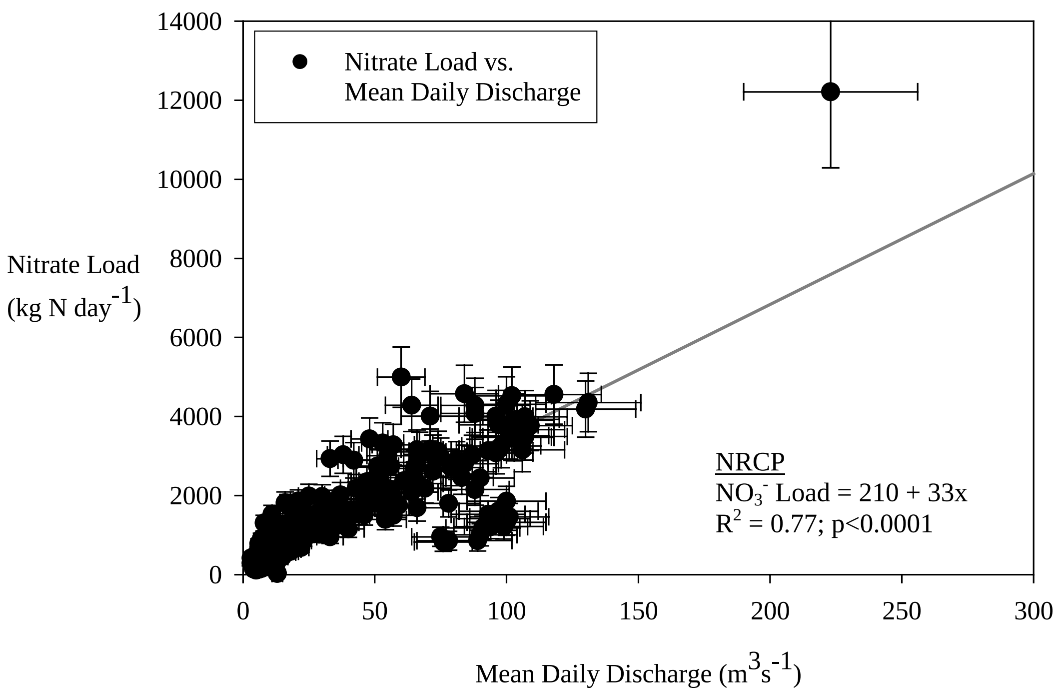


Figure 25. Relationships of nitrate load to average daily concentration and discharge at site NRCP 2001-02.

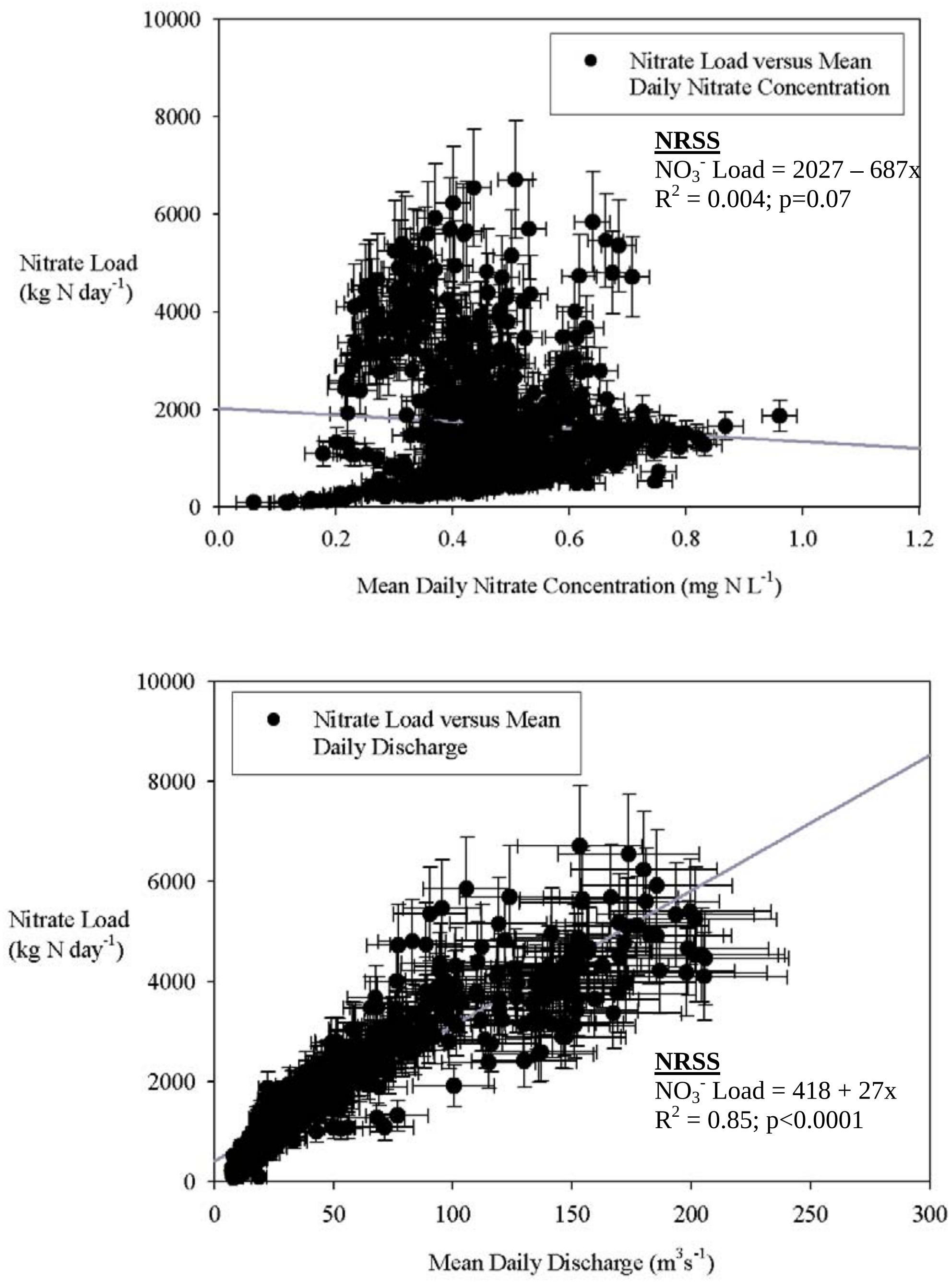
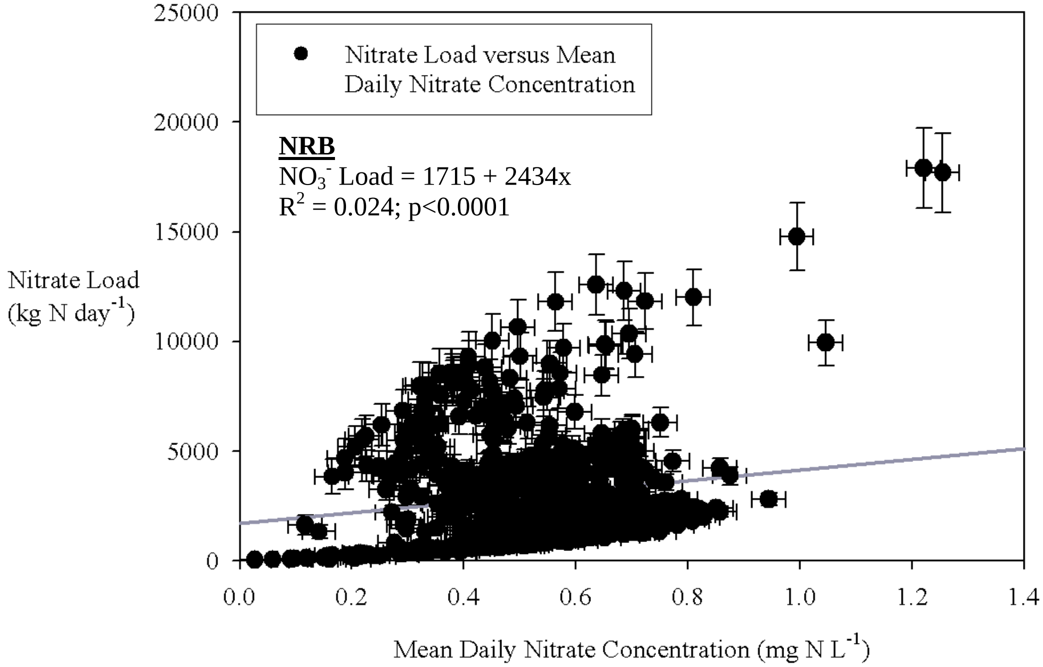


Figure 26. Relationships of average daily concentration and discharge to nitrate load at site NRSS 2001-02.



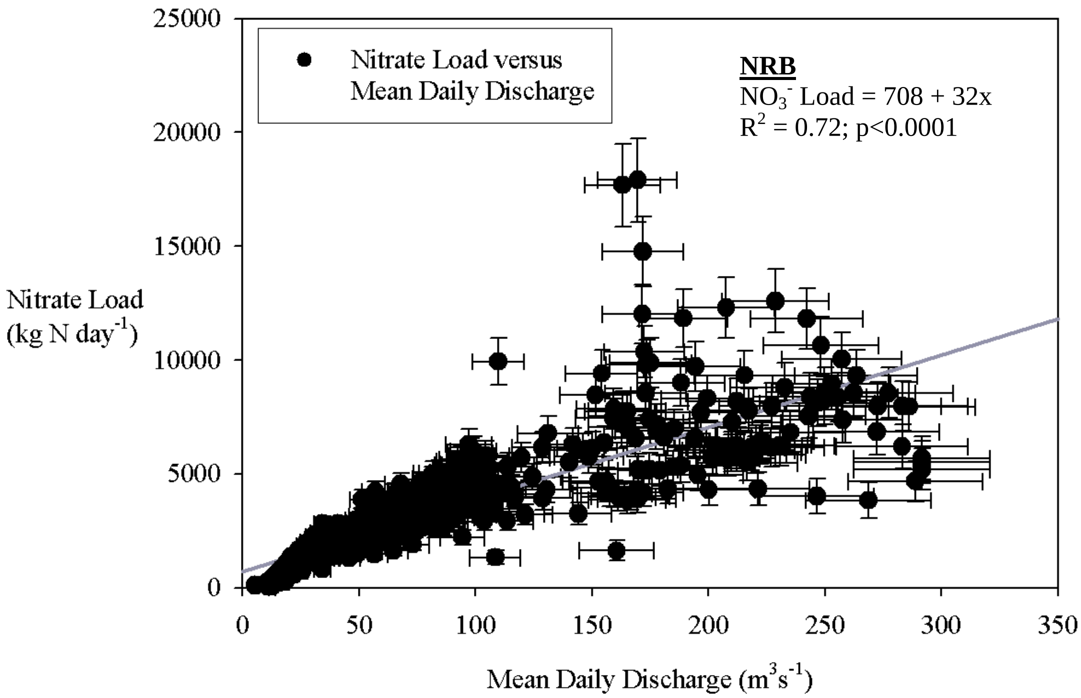
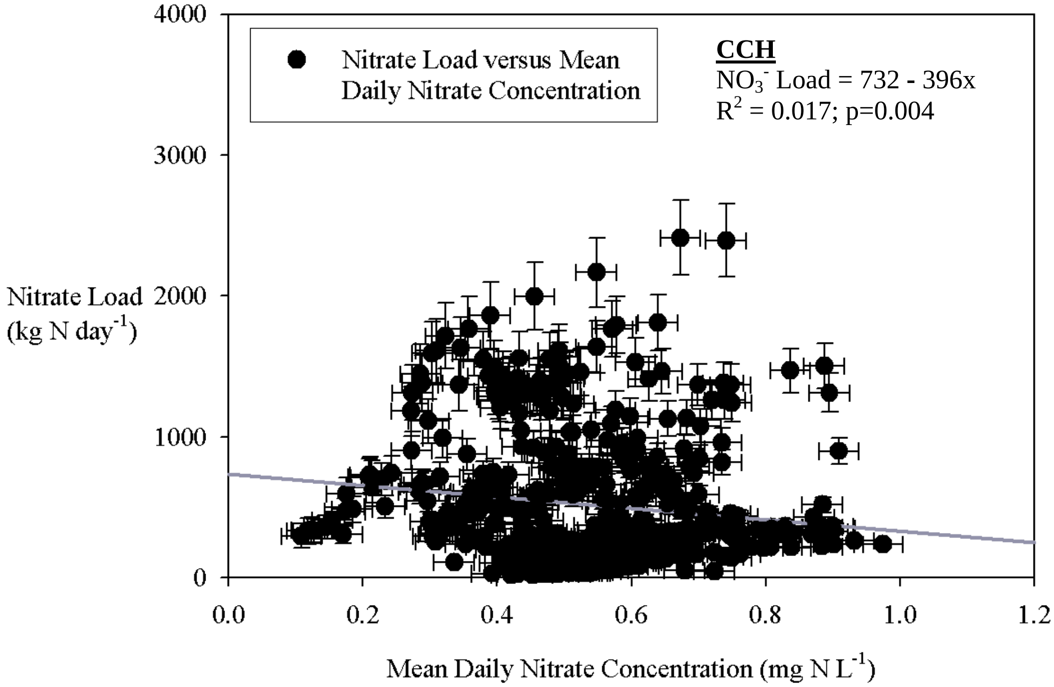


Figure 27. Relationships of average daily concentration and discharge to nitrate load at site NRB 2001-02.



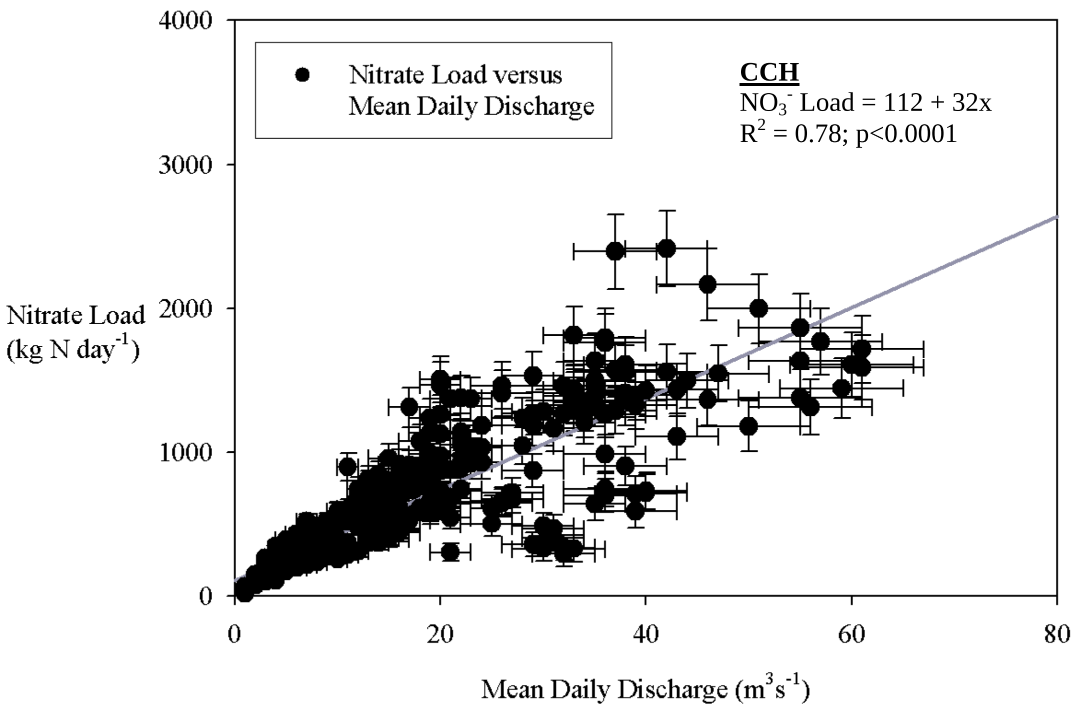
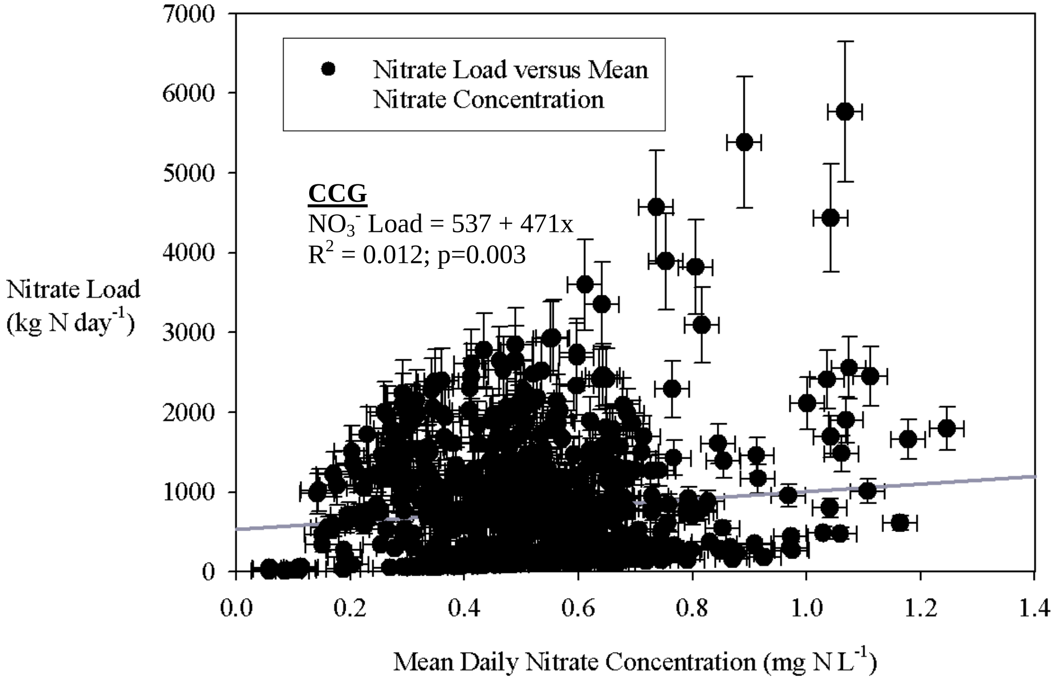


Figure 28. Relationships of average daily concentration and discharge to nitrate load at site CCH 2001-02.



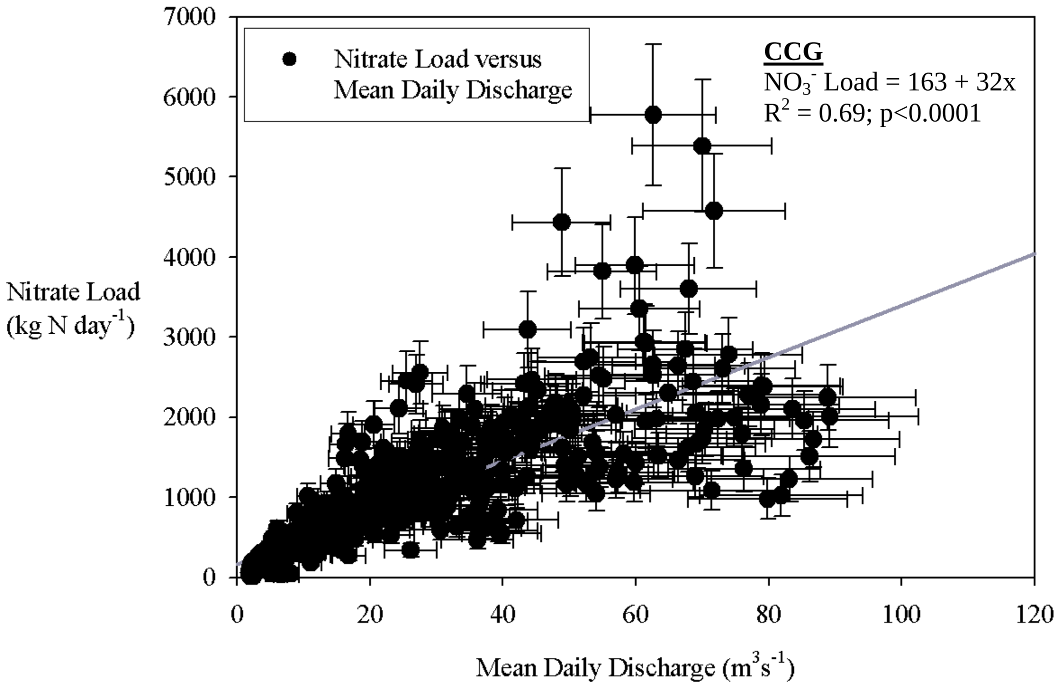


Figure 29. Relationships of average daily concentration and discharge to nitrate load at site CCG 2001-02.

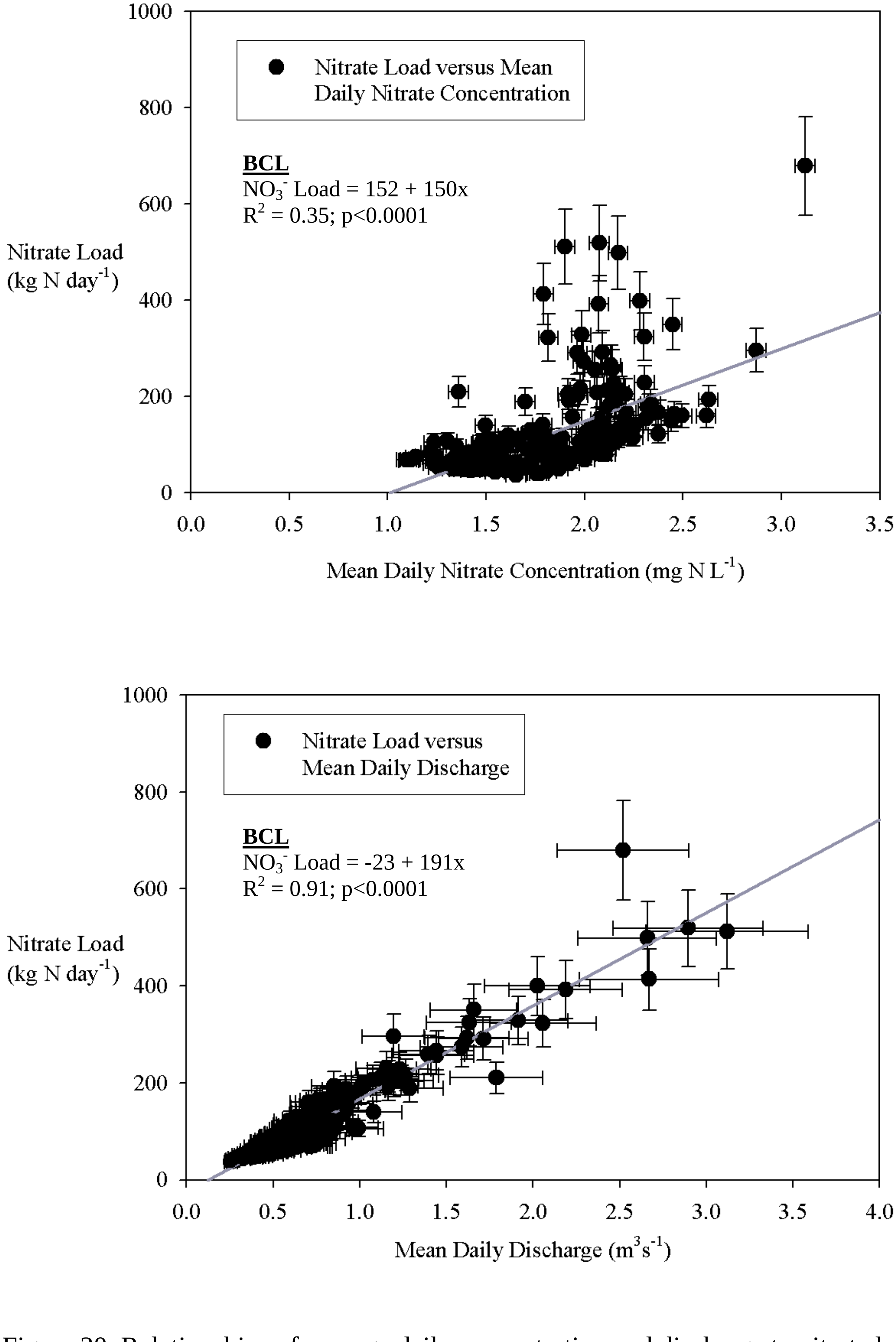
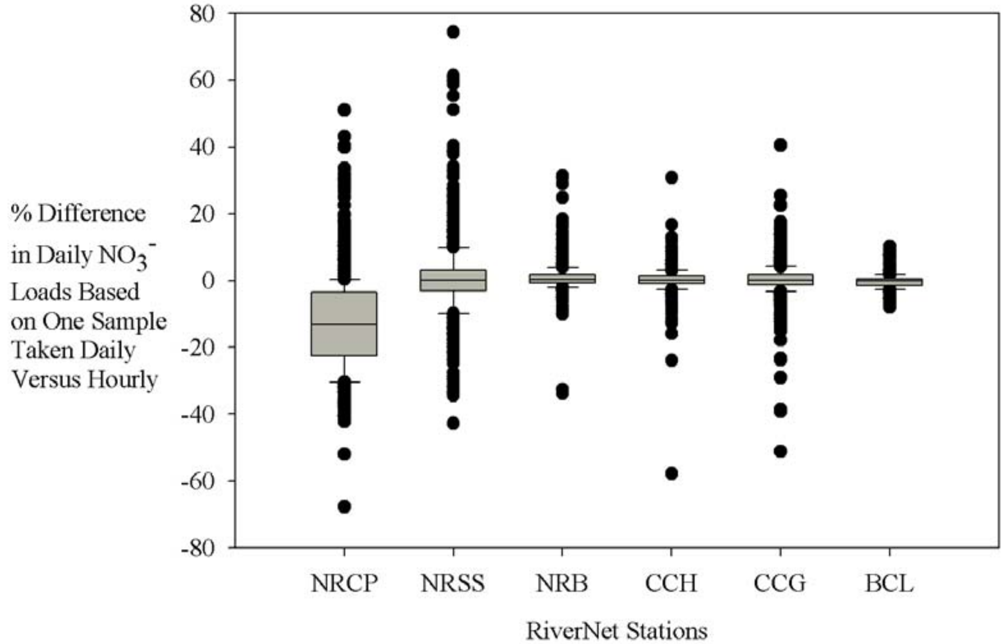


Figure 30. Relationships of average daily concentration and discharge to nitrate load at site BCL 2002.



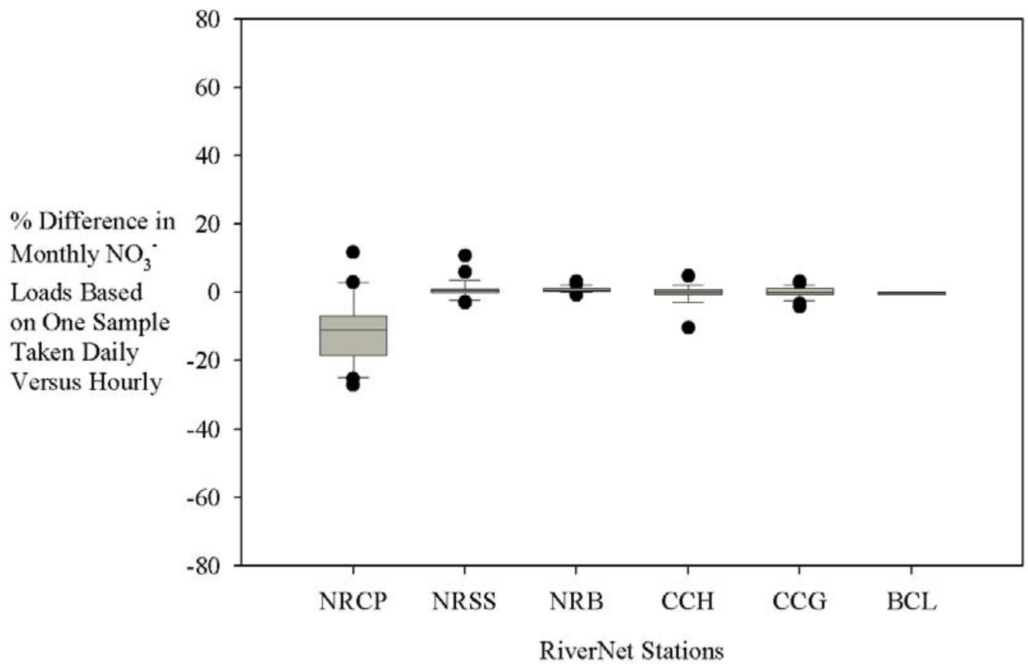
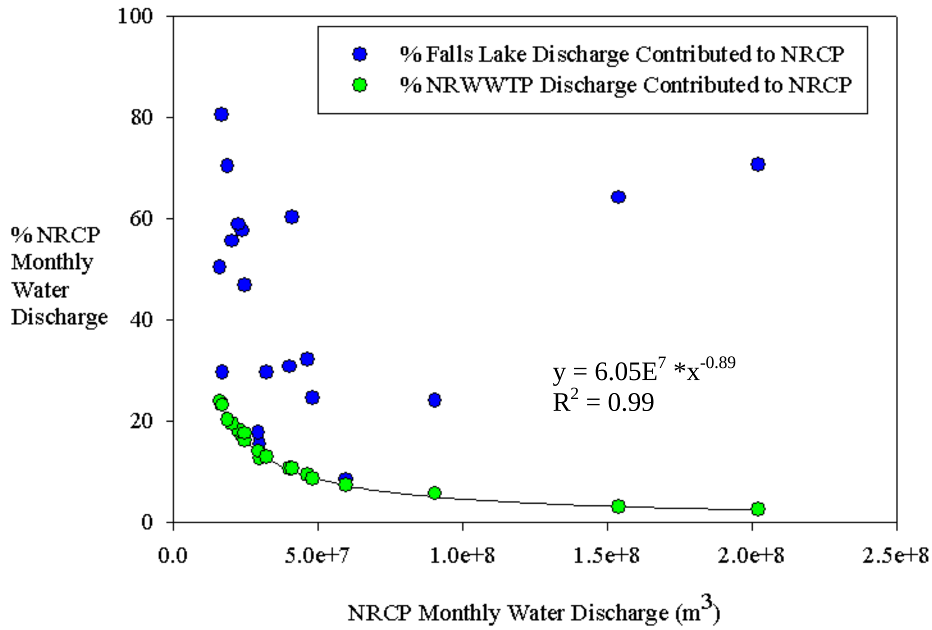


Figure 31. Difference in nitrate loads calculated from sampling nitrate concentration once a day versus hourly.



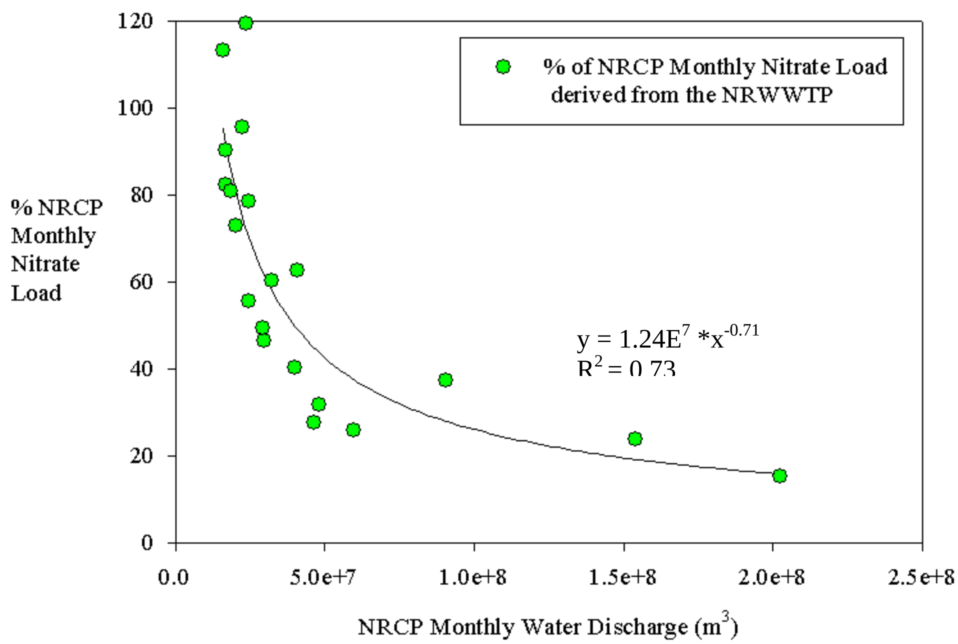
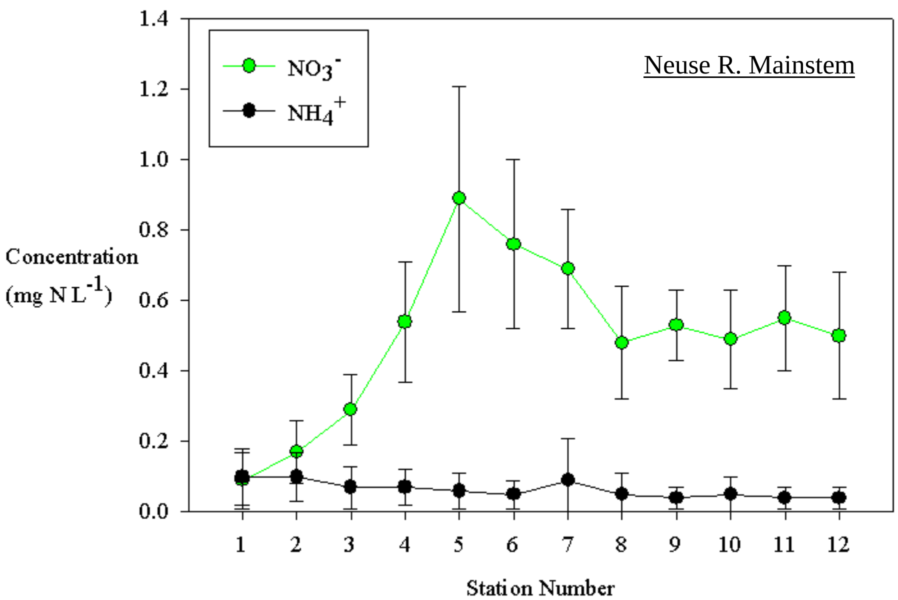


Figure 32. Influence of the Neuse River Wastewater Treatment Plant (NRWWTP) on monthly discharge and NO_3^- loads at site NRCP. NRCP monitored from May 2001 through December 2002. (USGS, 2001, 2002; CORPUD, unpublished data).



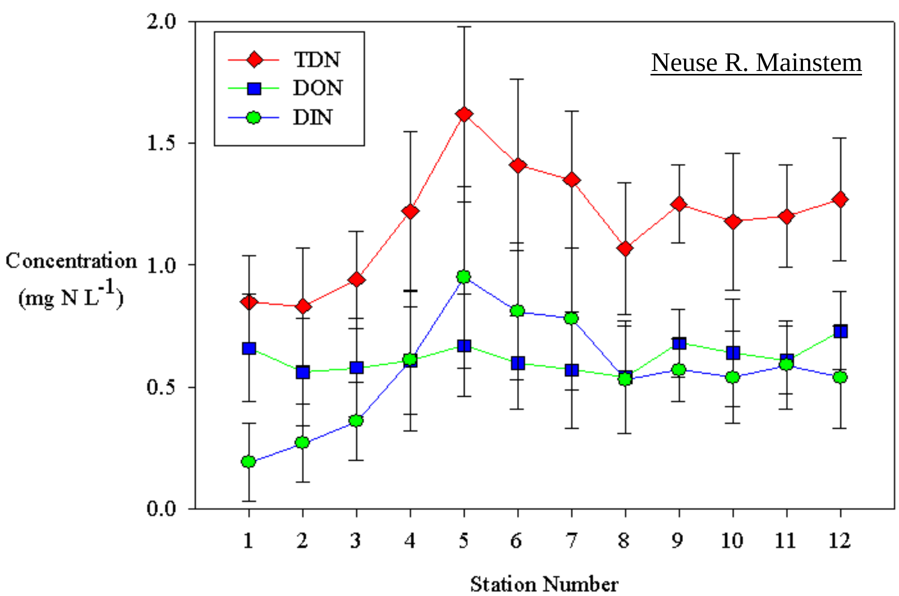
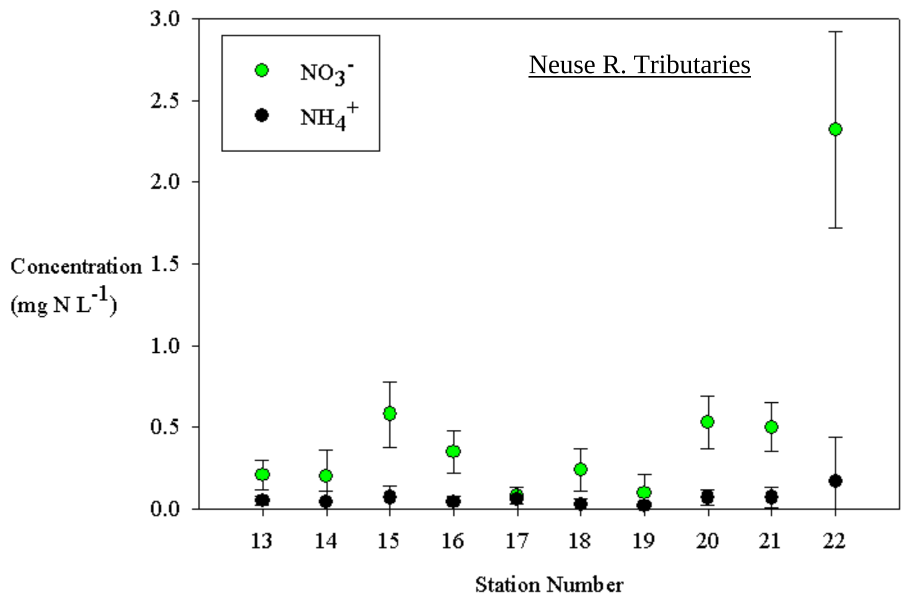


Figure 33. Nitrogen speciation in the Neuse River mainstem 2001-02. From FL (Station 1) to NRB (Station 12). Error bars indicate ± 1 SD of the mean concentration.



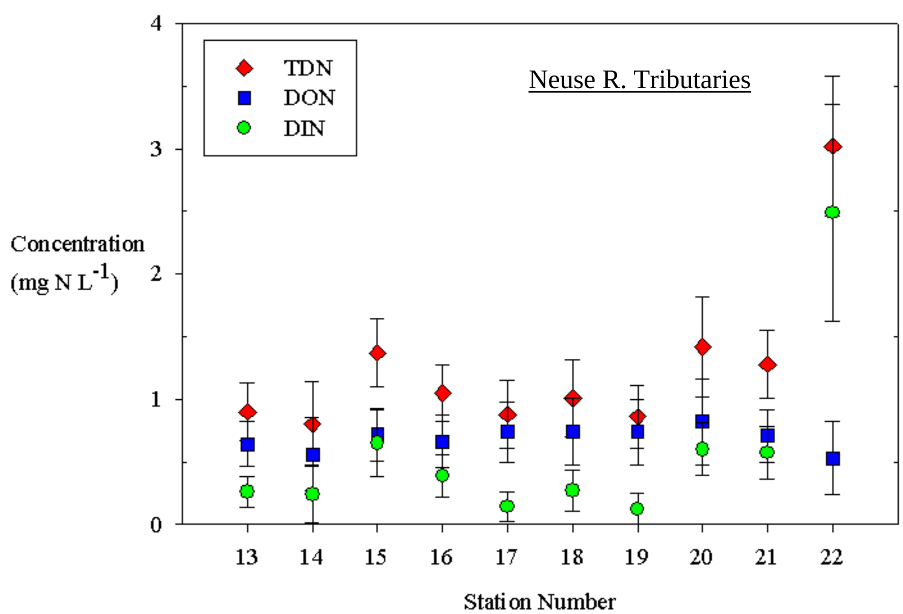


Figure 34. Nitrogen speciation in select tributaries in the Neuse River Basin 2001-02. Error bars indicate ± 1 SD of the mean concentration.

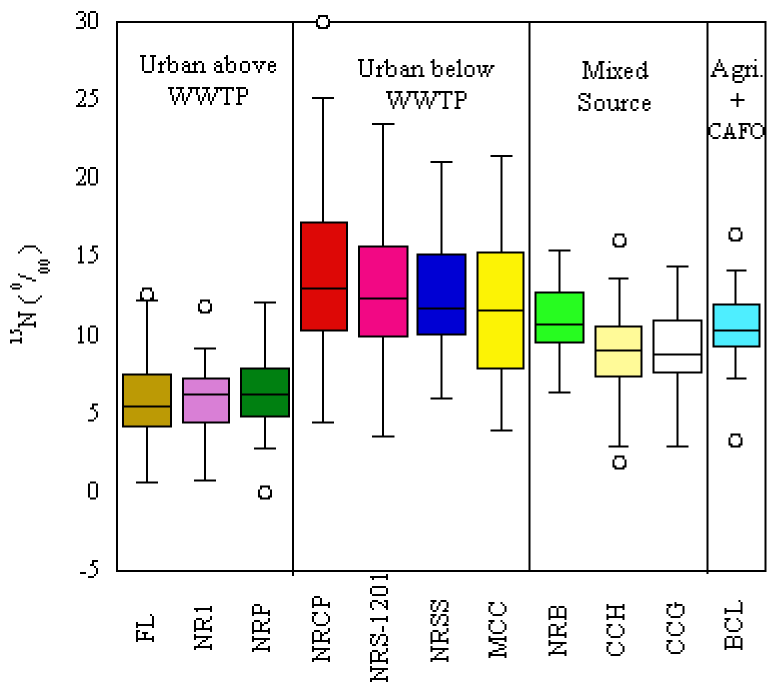


Figure 35. $\delta^{15}N$ for sites of different nitrate source input in the Neuse Basin 2001-02. Classifications based on upstream landuse and proximities to NPDES input.

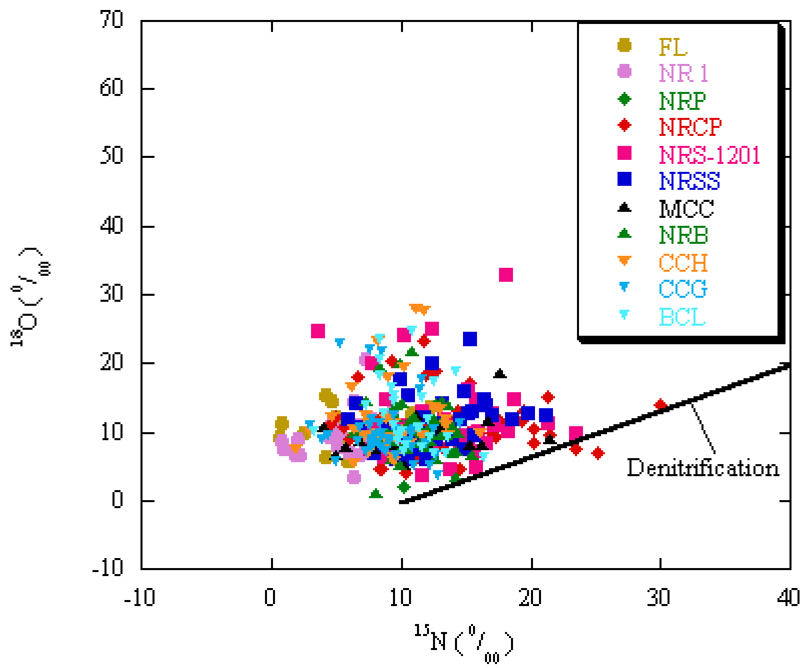
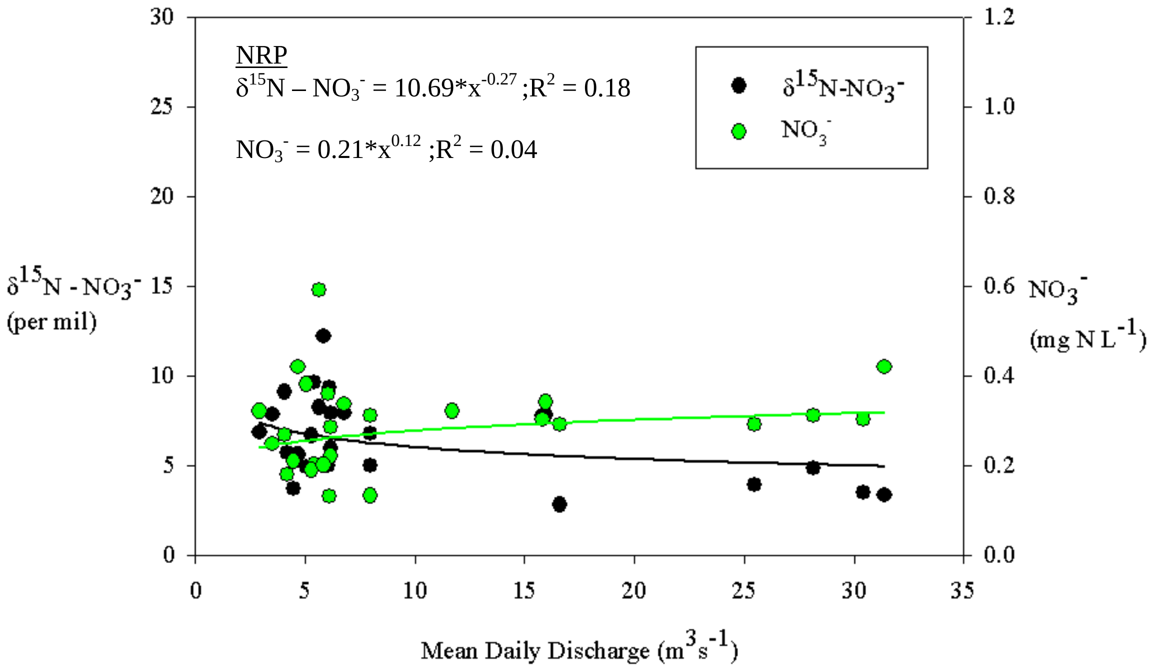


Figure 36. $\delta^{18}O$ and $\delta^{15}N$ for select sites in the Neuse River Basin 2001-02. Only a few samples fall along the denitrification line (Kendall, 1998).



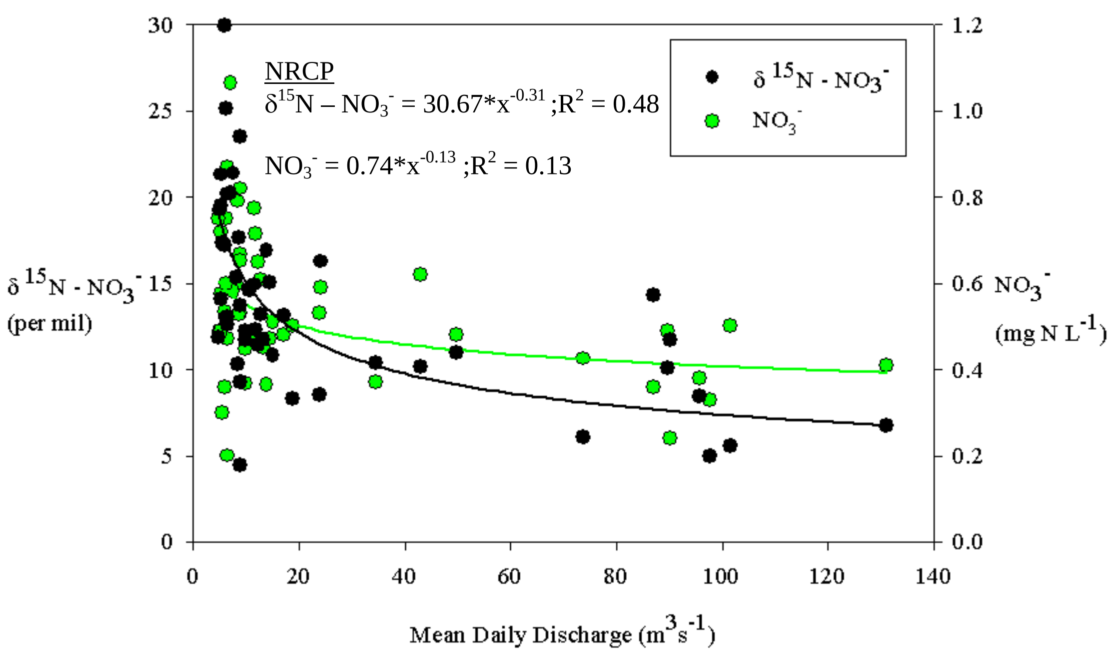
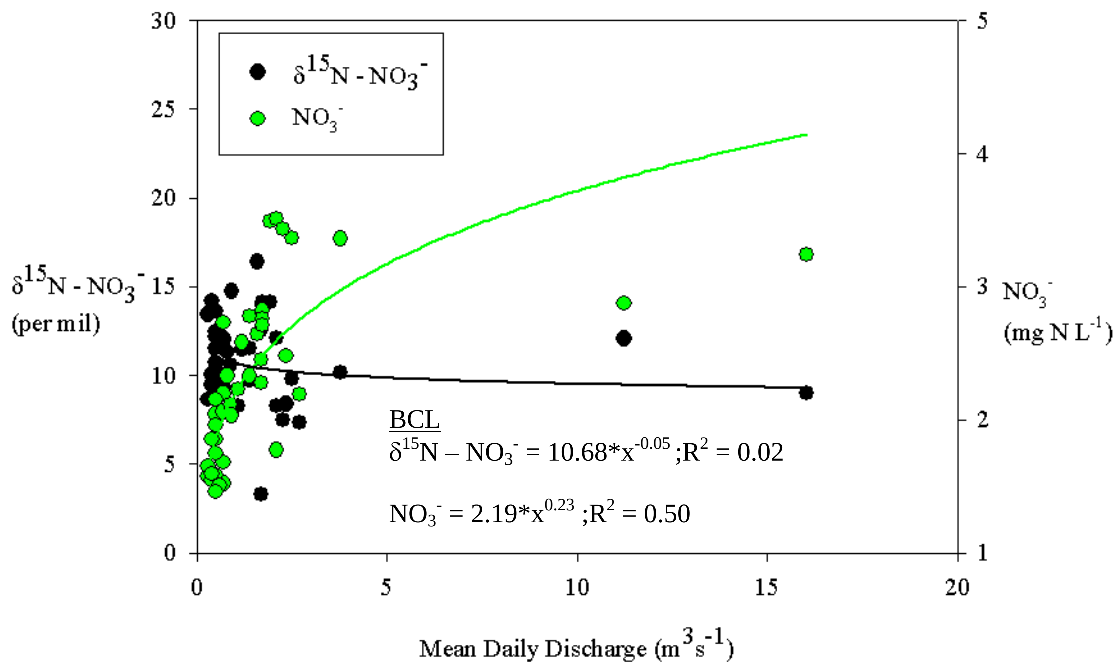


Figure 37. $\delta^{15}N$ and nitrate versus discharge at urban sites upstream (NRP) and downstream (NRCP) of the NRWWTP 2001-02.



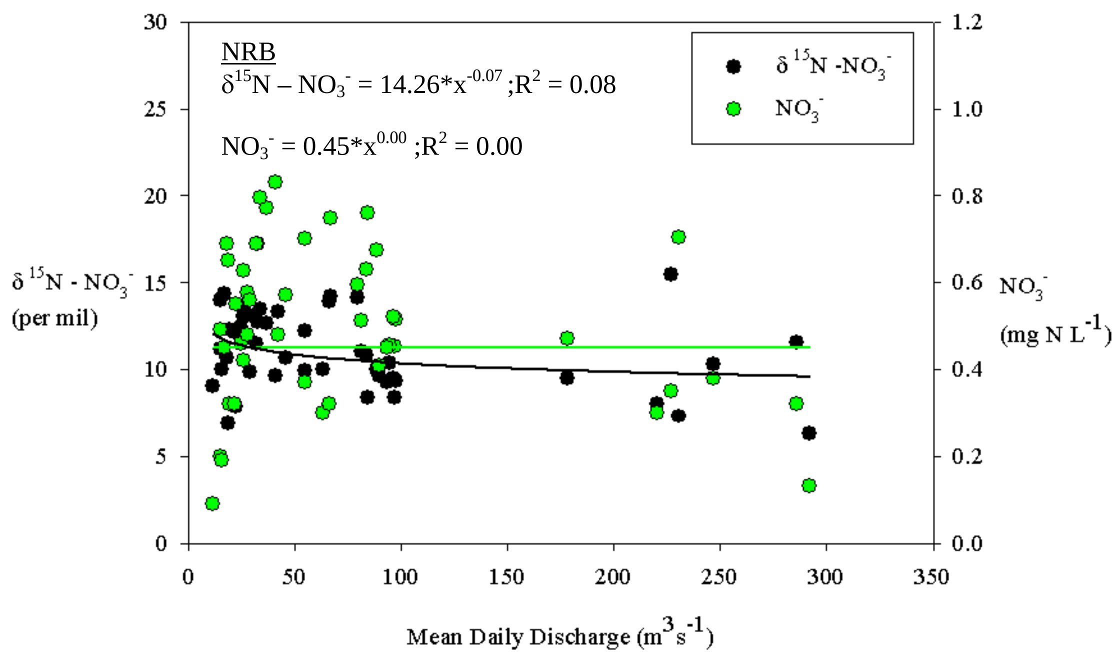


Figure 38. $\delta^{15}N$ and nitrate concentrations versus discharge at an agricultural (BCL) and mixed source site (NRB) 2001-02.

APPENDIX

APPENDIX. Measurements used for computation of depth-discharge equations.

Site	ADCP Measurement number	Date	Time	Station Depth (m)	ADCP Discharge ($m^3 s^{-1}$)	SD	Calculated Discharge ($m^3 s^{-1}$)	Percent difference from calculated	$2S_{mr}$ (95%)
NRCP	1	3/20/02	14:35-14:40	0.56	7.0	0.5	7.2	-2.9	15.1
	2	3/28/02	11:22-11:37	1.07	19.6	0.3	19.9	-1.4	8.6
	3	6/28/02	12:36-12:47	0.88	16.6	0.7	14.6	13.3	10.3
	4	7/26/02	9:45-9:49	1.31	27.6	0.6	27.5	0.4	7.3
	5	8/31/02	11:55-12:14	1.36	28.9	1.0	29.2	-1.2	7.1
	6	9/1/02	13:36-13:56	2.50	71.8	3.9	76.5	-6.2	8.7
	7	11/6/02	12:09-12:40	2.91	99.2	0.9	97.7	1.6	10.0
	8	11/19/02	11:45-11:52	2.71	82.1	0.9	87.0	-5.7	9.4
	9	1/7/03	11:14-11:33	1.94	47.7	2.3	51.1	-6.6	7.2
	10	5/2/03	10:21-10:32	3.45	120.4	2.0	128.0	-6.0	11.7
	11	5/6/03	11:36-11:50	1.66	31.2	0.5	39.9	-22.0	6.8
NRSS	1	12/19/01	14:46-14:56	0.72	15.1	1.1	14.7	3.2	16.3
	2	1/16/02	11:44-12:05	2.02	54.2	0.4	63.3	-14.4	8.1
	3	1/30/02	11:30-11:39	4.37	183.5	0.8	189.4	-3.1	11.5
	4	2/1/02	15:59-16:10	2.72	79.5	1.0	96.3	-17.4	8.3
	5	4/3/02	14:28-14:39	3.72	143.6	2.4	150.6	-4.7	10.1
	6	4/5/02	14:01-14:18	4.16	172.6	4.1	176.2	-2.1	11.0
	7	6/11/02	12:52-13:11	0.66	10.7	0.3	12.8	-16.4	17.3
	8	11/8/02	13:46-13:58	2.68	89.4	1.9	94.4	-5.3	8.2
	9	11/14/02	14:59-15:15	3.00	108.6	1.8	110.8	-2.0	8.7
	10	12/11/02	11:55-12:13	2.34	82.8	0.6	78.1	6.0	8.0
CCG	1	9/28/01	14:01-14:05	3.19	10.6	0.1	9.8	8.2	8.7
	2	12/19/01	12:20-12:27	2.75	5.1	0.5	4.3	17.1	11.9
	3	1/30/02	13:09-13:17	4.71	58.7	0.3	62.3	-5.8	10.6
	4	2/6/02	13:03-13:22	3.83	20.8	0.3	24.2	-13.9	7.8
	5	4/3/02	12:24-12:31	4.60	60.2	0.4	56.0	7.5	10.1
	6	5/30/02	11:37-11:57	2.52	2.2	0.2	2.6	-15.1	14.5
	7	8/29/02	12:46-12:56	2.69	3.8	0.2	3.8	0.9	12.5
	8	11/15/02	11:36-11:47	4.51	50.9	0.7	51.5	-1.2	9.8
	9	11/22/02	14:52-15:04	4.88	71.1	1.2	72.8	-2.3	11.2
	10	11/27/02	11:57-12:13	4.47	47.9	1.1	49.7	-3.5	9.6
CCH	1	9/28/01	11:23-11:44	1.56	10.8	0.2	10.3	4.8	5.0
	2	12/19/01	13:29-13:36	1.03	4.5	0.2	4.3	4.2	7.6
	3	2/1/02	14:37-14:43	3.03	45.1	0.4	46.9	-3.7	6.4
	4	2/6/02	14:43-14:57	1.83	13.6	0.3	14.8	-7.7	4.6
	5	4/3/02	13:15-13:21	2.76	36.8	1.0	37.6	-2.0	5.8

Site	ADCP Measurement number	Date	Time	Station Depth (m)	ADCP Discharge ($m^3 s^{-1}$)	SD	Calculated Discharge ($m^3 s^{-1}$)	Percent difference from calculated	$2S_{mr}$ (95%)
	6	6/7/02	13:13-13:27	0.68	1.9	0.1	1.9	-2.0	10.7
	7	10/15/02	14:24-14:37	2.13	23.7	0.4	20.8	13.9	4.6
	8	11/13/02	12:34-12:53	2.29	23.7	0.4	24.4	-3.0	4.8
	9	11/14/02	12:47-12:55	2.55	29.9	0.5	31.4	-4.7	5.3
	10	11/18/02	14:07-14:14	3.24	55.9	0.7	55.0	1.6	6.9
NRB	1	11/21/01	11:11-11:28	1.33	17.1	0.2	17.2	-0.6	11.1
	2	12/19/01	11:18-11:31	1.52	29.9	0.7	23.2	28.7	9.5
	3	1/16/02	13:55-14:16	2.83	95.2	1.9	98.0	-2.8	11.2
	4	2/6/02	11:21-11:44	2.96	92.1	0.8	108.5	-15.1	11.8
	5	4/3/02	11:31-11:44	3.33	139.1	1.4	142.0	-2.1	13.6
	6	4/9/02	11:01-11:14	3.70	168.7	2.2	181.4	-7.0	15.3
	7	5/29/02	12:09-12:50	1.36	15.0	0.3	18.0	-16.6	10.8
	8	7/3/02	16:16-16:34	1.23	19.3	0.3	14.3	34.8	12.2
	9	7/29/02	12:22-12:37	1.73	39.7	0.7	31.3	26.7	8.5
	10	9/6/02	12:09-12:36	2.80	90.5	1.1	95.1	-4.8	11.1
	11	11/22/02	13:08-13:27	3.72	178.3	2.2	183.5	-2.8	15.4
	USGS 1	6/13/01	15:45	1.85	35.7	n/a	36.8	-3.0	8.3
	USGS 2	7/24/01	13:15	1.44	22.5	n/a	20.7	8.9	10.1
	USGS 3	12/11/01	12:37	1.33	21.5	n/a	17.2	25.1	11.1
	USGS 4	6/25/02	16:15	1.12	13.1	n/a	11.4	14.6	13.7
	USGS 5	7/22/02	13:00	1.33	16.3	n/a	17.0	-3.9	11.1
	USGS 6	8/18/02	16:40	1.17	7.9	n/a	12.7	-38.2	13.0
	USGS 7	9/18/02	13:00	1.69	26.6	n/a	29.6	-10.1	8.7
	USGS 8	10/16/02	10:15	2.65	91.5	n/a	84.2	8.6	10.4
	USGS 9	12/9/02	14:15	3.11	111.3	n/a	121.9	-8.7	12.6