

Evaluating water quality in the lower Cape Fear: Effects on the health and survival of migratory fishes.

A.D. Goff and S.M. Brander

University of North Carolina, Wilmington
Biology and Marine Biology Department
601 South College Road
Wilmington, NC 28403
adg7759@uncw.edu
branders@uncw.edu

Acknowledgements

This literature review was made possible by funding from the National Oceanic and Atmospheric Administration. We'd like to thank The Nature Conservancy of North Carolina and NC Division of Marine Fisheries for making this research possible by providing UNCW the NOAA funds. Special thanks to Rebecca Brenner and John Hadley for their feedback and support throughout this research.

Table of Contents

Reference Guide for Acronyms	2
Abstract ...	3
Introduction ...	4-5
Nitrogen and Phosphorus ...	5-9
Harmful Algae Blooms ...	9-12
Other Pollutants ...	12-14
Climate Change and Anthropogenic Influences ...	14-16
Future Directions ...	16-17
Future Avenues of Research...	18
Figures...	19-20
Works Cited ...	21-24

Reference Guide for Acronyms

BOD – biochemical oxygen demand

CAFO – concentrated animal feeding operations

CF – Cape Fear

DENR – Department of Environment and Natural Resources

DO – dissolved oxygen

EDC – endocrine disrupting compound

FMP – fisheries management plan

GV – Guideline Value

HAB – harmful algae bloom

LC – lethal concentration

LD – Lock and Dam

MC – microcystin

NOAA – National Oceanic and Atmospheric Administration

POP – persistent organic pollutant

TDI – total daily intake

TNC – The Nature Conservancy

WHO – World Health Organization

Abstract

*Excessive loading of nutrients (such as nitrogen and phosphorus), presence of persistent pollutants, and occurrences of harmful algae blooms are becoming increasing concerns for freshwater and marine ecosystems. The Cape Fear River (CF) in North Carolina, which is accustomed to heavy nutrient loading and is a catchall for runoff from drainage basins throughout the state, is no exception. The delivery routes of harmful and noxious chemicals into the environment and the associated effects on exposed aquatic communities are poorly understood, particularly with regards to important migratory fish species. For example, the status of economically important CF fisheries, such as American shad (*Alosa sapidissima*), Atlantic and shortnose sturgeon (*Acipenser oxyrinchus* and *A. brevirostrum*), and striped bass (*Morone saxatilis*), can be impacted by these changes to water chemistry, as can drinking water quality. In particular, special attention has been raised by the appearance of cyanobacteria (blue green algae) blooms in the CF during drought events, worsened by eutrophication of surface waters from terrestrial runoff. This review incorporates current literature to examine the sources of nutrient loading and receipt of other anthropogenic pollutants to the river, effects of resultant harmful algae blooms on fish health, and proposes management strategies for the future to maintain safe water quality practices and therefore improve fish health.*

Introduction

Anthropogenic addition of nutrients, pesticides, wastewater, heavy metals, and other pollutants are changing aquatic habitats and as a result, impacting fishes in our rivers and streams throughout the world (Lintelmann 2003). Nutrients, hormones, and trace elements essential to maintaining homeostasis are closely regulated by aquatic organisms to promote optimal function. Alterations to the available levels of nutrients, in concert with other anthropogenic inputs, have a wide range of adverse effects on fishes (Crain et al. 2008; Vinodhini and Narayanan 2008; Brander 2013).

The Cape Fear River (CF), the largest river system in North Carolina, is no exception to these ecological impacts. Classified as a Piedmont, or brown water, river (Mallin pers. comm.), the CF is accustomed to heavy nutrient loading and being a catchall for water runoff from drainage basins throughout the state. Over the past several decades, intensification of agriculture, concentrated animal feeding operations (CAFOs), changes in the population density of communities located within the river basin, and increasing coverage by impervious surfaces have drastically changed the surface runoff and resulting nutrient profile of CF aquatic communities (Mallin 2009, Viehman 2011, Griffin 2013). Despite these changes, the river remains a critical resource for people and for biodiversity. The land surrounding the CF, known as the Cape Fear Arch, is distinguished by unique geology and the greatest biodiversity on the Atlantic Coast north of Florida. Running from Cape Lookout, N.C. to Cape Romain, S.C. and extending inland to Fayetteville, N.C., the Cape Fear Arch has remained above sea level for a longer period of time than surrounding regions (Smith 2010). The slight advantage in elevation allowed the development of a variety of wet and dry habitats that gave rise to unique natural communities and promoted diversification of plants and animals.

Anadromous (or migratory) fish species, representatives of the CFs broad diversity, spawn in freshwater but spend majority of their adult lives in marine waters (Williams and Moser 2000). The CF once supported thriving populations of migratory fish, including American shad (*Alosa sapidissima*), Atlantic and shortnose sturgeon (*Acipenser*

oxyrinchus and *A. brevirostrum*), and striped bass (*Morone saxatilis*). Migratory fish populations in the CF have declined substantially over the past century, with commercial landings 87% lower than historical estimates (Cape Fear River Basin Action Plan for Migratory Fish 2013). The economic value of recreational fishing on the CF was valued at \$1,663,000 in 2009 (NCDENR 2009), showing that restoration of fish stocks improves the ecology of the river and economy of the state.

Action is needed to improve water quality and to aid in the restoration of important migration routes for recreational and commercially significant fish stocks in the CF. Overfishing, impaired water quality, and obstructions to migration routes can adversely affect the health of fisheries by reducing recruitment (number of juveniles that become reproductively mature adults) and diminishing reproductive success (less young being produced lead to fewer adults) (Burdick and Hightower 2006). Atlantic and shortnose sturgeon (*A. oxyrinchus* and *brevirostrum*) are particularly sensitive to overfishing due to late age of female maturity. As such, female sturgeon must endure 19 years of fishing pressure before they are able to reproduce (Williams and Moser 2000).

Nitrogen and Phosphorus

Nitrogen (N) and phosphorus (P) are naturally occurring elements in rivers and bodies of water, but anthropogenic inputs to aquatic systems can artificially increase or decrease the available concentrations of these nutrients. The main stem of the CF is a fifth order stream, and is considered a Piedmont, or brown water, river that is joined by two fifth-order blackwater streams (Black and Northeast CF). The difference between a blackwater and Piedmont (brown water) river is that Piedmont rivers receive clay turbidity loading (Mallin pers. comm.). During periods of heavy rainfall, terrestrial sources transport nitrogen and phosphorus into tributaries that eventually deposit excessive nutrient loads to the main river body. Surface runoff and ground water transported from CAFO lagoons are additional sources of input (Paerl 2010).

Anthropogenic nitrogen is transported to the river as runoff from agricultural fertilizers and waste products. Traditionally levels of biologically available nitrogen are microbially

mitigated through the processes of denitrification and anaerobic ammonium oxidation (anammox) (Hines 2012). Nitrogen loading to nitrogen-limited waters can cause hypoxia and noxious algal blooms (eutrophication), mortalities in fish and macroinvertebrate communities, and outbreaks of harmful aquatic organisms (Costanza 2008). These scenarios will ultimately lead to decreases in water quality (including high levels of organic matter and low dissolved oxygen levels from decomposing bacteria) resulting from the decomposition of deceased organisms. There is a fine line between triggering harmful algae bloom events (HABs) and restricting phytoplankton growth contingent on the amount of available nitrogen and phosphorus. Restricted phytoplankton growth causes problems throughout the food web, since decreasing the biomass of autotrophic and heterotrophic microorganisms eliminates vital food sources for larger inhabitants of the river such as fishes (Heisler 2008).

Phosphates are the most common form of phosphorus and are generally limited in abundance, acting as a limitation on plant growth in aquatic environments. Phosphate is a constituent of DNA, RNA, ATP (cells' energy source), and phospholipids (building blocks for all cell membranes) (Schindler et al. 2008). Intuitively it would seem that more phosphate would be advantageous to aquatic ecosystems by promoting new levels of cellular development and growth, however, this not the case. Unfortunately, cyanobacteria, many species of which are toxic, are capable of making better use of available phosphorus than more complex aquatic plants (Jang 2007). This allows them to dominate during periods of excessive nutrient loading.

Dependent on rates of flow, levels of eutrophication are not consistently distributed throughout the river. Biogeochemical processes are responsible for the reduction of inorganic nutrients as water moves downstream (Webster et al. 2003). Peterson et al. (2001) proposed that tributaries and small streams collect most of the dissolved nutrients from terrestrial ecosystems. Collected data on N transport from this study suggests that tributaries and smaller streams are most effective in N processing and retention.

Water quality data for nutrients in the Lower and Middle CF is plentiful and groups like The Nature Conservancy (TNC), National Oceanic and Atmospheric Administration (NOAA), and the Department of Environment and Natural Resources (DENR) are analyzing available data and building models using this data. These models are being constructed with the intention of better understanding nutrients and their sources to enable better conservation of fish and river health. Phosphates are not toxic to fish, although they do promote algal blooms, but nitrogen in its various forms does have toxic effects on fish (ammonia and nitrite are most toxic, nitrate and ammonium are least toxic). A study by Camargo and Alonso (2006) established that levels of total nitrogen lower than $500 \mu\text{g l}^{-1}$ to $1000 \mu\text{g l}^{-1}$ could prevent acidification and eutrophication of freshwater systems, protecting aquatic animals (citing fluctuations based on temperature variation). From June 2002 to July 2003, sampling sites between Lock and Dams 2 and 3 (LD2 and LD3) (see Fig. 1 for locations and inputs) indicated elevated concentrations of dissolved inorganic nitrogen (DIN) and soluble reactive phosphorus (Dubbs et al. 2008). For migratory fish, the persistence of elevated nutrient levels in the main stem of the river may be causing disruptions to chemosensory cues (Fig. 2) that have historically provided navigation towards established spawning sites (Foster 1985; Keefer et al. 2013). In other words, fish have a natural instinct for locating good spawning grounds and elevated nutrients can interfere with this ability. With differences in landscape contributing to water quality variables (Zhang 2014), migratory fish may be wrongly pursuing alternate routes that wind up being dead ends. Fish depleted of energy reserved for spawning, can result in mortalities and aborted reproductive events (Moore and Waring 2001).

A suspected source of nutrient input to the CF below Lock and Dam 1 (LD1) is specific to the 2,125 CAFOs (Constanza 2008) located in the coastal plain region of North Carolina. Mallin et al. (2003) report that an estimated 124,000 metric tons of nitrogen along with 29,000 metric tons of phosphorus are generated annually by CAFOs in this state. The same study suggests the main forms of delivery of that nitrogen include runoff, percolation into ground water, and volatilization of ammonia. The Middle CF is

dominated by inputs from point and non-point sources. Point sources are distinct conveyances such as pipes or man made ditches. Nonpoint sources result when rainfall, irrigation and septic systems, or snowmelt runs over land or through the ground, picks up pollutants, and transports them to surface or ground waters (epa.gov). According to Ensign (2006), storm events are responsible for 72% of nitrates (NO_3^-) and 82% of phosphates (PO_4^{3-}) that are attenuated in the river system (primarily from nonpoint sources). These inputs are responsible for fish kills, algal blooms, microbial contamination and countless other ecological complications. However, there are novel approaches being developed to tackle issues of eutrophication. For example Wang et al. (2012) proposed improving nutrient concentrations and inhibiting cyanobacteria growth by supplemental regulation of N and P levels through the introduction of macrophytes (aquatic plants) to affected waterways.

a. Ammonia, nitrates, and nitrites

Ammonia, nitrate and nitrite are all capable of exerting harmful effects on fish health. Increased concentrations of ammonia in bodies of water can cause imbalances in osmoregulation, leading to kidney failure, and can cause suffocation through damage to gill epithelium (Hrubec 1996) (Fig 2). In the CF from 1990 to 1999, ammonia levels ranging from $30\mu\text{g l}^{-1}$ to $150\mu\text{g l}^{-1}$ were established from a sampling station at LD1 (Bales et al. 2000). Eddy (2005) established sublethal ammonia concentrations in blood plasma for 32 species of freshwater fish ranging from $2.55\mu\text{g l}^{-1}$ to $5.11\mu\text{g l}^{-1}$. Ammonia is naturally introduced to aquatic ecosystems as the main nitrogenous excretory product of fish. Through a process known as nitrification, ammonia is broken down by bacteria and forms nitrate as a product of oxidation. Laboratory investigations by Oppenborn et al. (1993) established mean lethal concentration (LC_{50}) values for juvenile striped bass (*M. saxatilis*) as 770 to $1250\mu\text{g l}^{-1}$ of ammonia.

Nitrates and nitrites that persist in the environment represent inorganic sources of nitrogen (IN). Hrubec (1996) demonstrated preliminary evidence from striped bass that suggested blood electrolyte chemistry, immune and pathologic response, and decreased

antibody production may all be effects of exposure to elevated nitrate concentrations. Eddy (2005) wrote that in the presence of elevated nitrogen migratory fish swimming upstream do not eat sufficient amounts, end up with elevated blood ammonia levels, and are more susceptible to being harmed by ambient ammonia. This study documented side effects of ammonia exposure as decreased growth rate and increased plasma cortisol levels over 84 days compared to control (Fig. 2).

Elevated levels of nitrite can cause methemoglobinemia (brown blood disease) in fish, which results in a decreased capacity for carrying oxygen. Although very little research has been conducted on the effects of elevated concentrations of nitrogenous compounds on juvenile and developing fish, the impact on fry and juvenile fish is likely much more severe and shorter in onset than on adult fish (Hrubec 1996). As such, migratory fish could be putting their progeny at a further disadvantage by spawning in an area that is highly contaminated by elevated concentrations of nitrogenous substances.

Harmful Algae Blooms

According to Heisler (2008), harmful algal blooms (HABs) can be considered as potentially toxic autotrophic or heterotrophic species and high biomass producers capable of causing hypoxia, anoxia, and mortalities of marine life at certain concentrations. Depending on the concentrations of toxins and algal species associated with HABs, mortalities of terrestrial organisms can result after drinking from areas of concentrated toxins (Carbis 1997). The important distinction amongst different algal bloom events pertains to the presence of toxic or non-toxic species. Regardless of toxin presence, bloom density can block light to the freshwater system impeding autotrophic productivity and depleting dissolved oxygen (DO) levels via cell death and decay. Blooms can be triggered by excessive nutrient loading which allows them to replicate at an incredibly high rate (one or more divisions per day; Heisler 2008). Blooms are capable of physically devastating commercial fisheries from the sheer accumulation of

biomass alone, since often times fishing gear and nets are compromised or destroyed because of the weight of the algae.

Blooms are an issue within the CF as a result of heavy nutrient loading, particularly phosphorus and nitrogen. For example, the area above LD1 has experienced four HABs of *M. aeruginosa* in the period from 2009-2012 likely due to a combination of increased surface temperatures and low flow rates (Mallin 2014). Specific measurements made by Isaacs et al. (2014) in the fall of 2009 and summer of 2012 document the density of two bloom events that occurred just below LD 1. Using *chl a* as an indicator of biomass, densities were calculated for the fall and summer at $64\mu\text{g l}^{-1}$ and $441\mu\text{g l}^{-1}$, respectively. According to the World Health Organization (WHO), *chl a* concentrations of $50\mu\text{g l}^{-1}$ indicate a moderate risk algae bloom (Chorus and Bartram 1999). The algal blooms observed by Isaacs et al. would qualify as a moderate and significant bloom, respectively.

The newly instituted Rock Arch Rapids located at LD 1 has not been established long enough to be associated with promoting or deterring bloom events. The original LD 1 was replaced by the Rock Arch Rapids system to assist the passage of migratory fish up the river. A study by Burdick (2006) reports that anadromous fishes will utilize upstream spawning habitat liberated by dam removal. The foreseeable dangers of the new Rock Arch setup are thorough mixing of the water column, providing nutrients from depth to algae blooms, and spreading of microcystins (type of toxin produced by some species of cyanobacteria) during toxic bloom events via the rupturing of toxin containing algae cells as they make their way down the rapids (Figueiredo 2004).

a. Cyanotoxins

Cyanotoxins are harmful compounds that are produced by toxic strains of cyanobacteria. These toxins are generally divided into three categories: dermatoxins (skin irritant), neurotoxins, and hepatotoxins (liver toxicity). One group of hepatotoxins produced by the algae *Microcystis aeruginosa*, microcystins (MCs), receives special attention because they are capable of acute poisoning and are potential carcinogens.

Most MCs are water-soluble, which aids in dispersal and bioavailability to aquatic organisms. Figueiredo et al. (2004) reported microcystin-LR to be the greatest cancer promoter of known microcystins (>80 strains). A recent study by Isaacs et al. (2014) reports that subtoxic levels of MCs can exhibit endocrine disrupting effects as well as cause genetic mutations. In addition to the documented toxicity of MCs, Isaacs et al. (2014) have discovered two new micropeptin cyanopeptides that are suspected of having toxic effects similar to MCs, but further investigation is required. The Guideline Value (GV) for total microcystin-LR in drinking water has been established by the WHO as $1\mu\text{g l}^{-1}$ (Codd 2000). The symptoms of the toxic effects of MCs in humans include nausea, vomiting, fever, sore throat, eye and ear irritation, visual disturbances, myalgia, acute abdominal pain, and kidney and liver damage (Isaacs et al. 2014). MCs also disrupt protein phosphatases in the liver, which are important for cell signaling (Codd 2000).

The effect of MCs on fish health is currently being investigated but at the present is not well understood. A study by Carbis (1997) documented cases of hepatocyte atrophy in 66% and gill necrosis in 37% of carp (*Cyprinus carpio*) sampled from two Australian lakes experiencing bloom events. Additional observations made by Carbis (1997) included epithelial ballooning, folded lamellar tips, and exfoliation of lamellar epithelium (Fig 2). Collected specimens were found to be experiencing difficulties associated with anion/cation homeostasis and respiratory complications, however, no mortalities of adults were reported.

The Carbis study may be an exaggerated case since it is possible that carp were utilizing *M. aeruginosa* as a large portion of their diet during the bloom event, causing above average accumulation of microcystins. Nevertheless, bioaccumulation of microcystins in organisms that show no sign of duress or impairment could be disastrous for commercial and recreational fishermen and their clientele on the CF. A study by Magalhaes et al. (2001) investigating MC contamination in a freshwater lagoon in Brazil found 71.7% of fish tissues sampled were above the total daily intake (TDI) value for MC

(0.04 $\mu\text{g kg}^{-1}$). Careful monitoring of catch during bloom events is required to avoid health complications from consuming contaminated fish.

Water treatment systems need to be evaluated to ensure that proper screening and filtration methods are being utilized to maintain the GV for MCs in our drinking water and to maintain ideal conditions for fishes. Hitzfeld (2000) suggests that ozonation, dechlorination, and micro/ultra filtration are effective techniques for microcystin filtration and removal. It should be noted that these techniques may not be sufficient during bloom events or periods of high organic loading. Ferrate oxidation-coagulation and Fenton oxidation of MC-LR using Fenton reagent have been documented as promising methods for degradation of these hepatotoxins during periods of high organic carbon loading (Gajdek et al. 2001 and Yuan et al. 2002). Figueiredo et al. (2004) observed a reduction in ozonation effectiveness from high total organic carbon loading and high cyanobacterial densities. Ozonation is responsible for causing cells to lyse and thus increasing dissolved MC levels. Suggestions for improving treatment of MC laden waters involve flocculation (slow sand filtration), for removing cell-bound MCs, and activated carbon absorption (wood-based carbons being most effective) in addition to ozonation, for removing dissolved MCs (Figueiredo et al. 2004).

Not all strains of *M. aeruginosa* are toxin producing, making it important to identify specific strains during bloom events to determine appropriate actions in case of a highly concentrated toxic bloom. Many times blooms are co-dominated by multiple strains making a single diagnosis difficult to achieve (Jang et al. 2007). Jang et al. (2007) observed an increase in MC production by toxic strains of *M. aeruginosa* as an allelopathic (inter-species competition) response to the presence of non-toxic strains of *M. aeruginosa* offering the toxic strain a competitive advantage. Similarly, MC production was increased in response to the presence of planktivorous fish (silver carp, *Hypophthalmichthys molitrix*) suggesting MC production is an inducible defense to the presence of fish (Jang et al. 2004).

Other Pollutants

Sources of pollution for additional consideration include: endocrine disrupting compounds (EDCs), persistent organic pollutants (POPs), and marine debris. Persistent organic pollutants, many of which interfere with hormone function (endocrine disruptors), are organic compounds resistant to chemical, biological, and photolytic degradation in the environment. According to the EPA's Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC), an endocrine disruptor is "an exogenous chemical substance or mixture that alters the function(s) of the endocrine system and thereby causes adverse effects to an organism, its progeny, or (sub) population" (Lintelmann 2003). Their persistence in natural environments can lead to bioaccumulation in human and animal tissues, as well as in food webs, causing significant impacts to aquatic communities and human health (Brander 2013; Ritter 1995). For example, perfluorinated compounds (PFCs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are known POPs that can also act as endocrine disruptors. The North Carolina Division of Water Quality (<http://www.ncwaterquality.org>) recommends drinking water not exceed a PFOA concentration of 40 ng/L. Alarming, an evaluation of surface waters in the CF found 32% of sampled sites had PFOA levels greater than 40 ng/L (Nakayama et al. 2007). Laboratory investigations using the rare minnow, *Gobiocypris rarus*, conducted by Wei et al. (2008) identified a number of genes that were up-regulated or down-regulated in response to PFOA exposures using cDNA microarrays. The study found that lipid metabolism and transport, hormone function, immune response, and mitochondrial function were all affected by PFOA exposure at the lowest concentration administered (0.3 mg l⁻¹). Further study is needed to determine the impact of trace concentrations of PFOA and other endocrine disruptors on fish health.

A study by Palumbo et al. (2009) suggests that sturgeon are more susceptible than other anadromous fishes to EDCs since they take 10 to 20 years before they reach sexual maturity (Fig. 2.). Increasing concentrations of pesticides and pharmaceuticals in

agricultural runoff and wastewater, and hormones in effluent originating from CAFOs, have been shown to alter hormone levels, interfere with gonadal development, reduce fecundity, and alter sex ratios in fishes (Brander 2013). For example, pyrethroid pesticides, which have become increasingly popular for urban and agricultural use, have been shown to effect the expression of estrogen-mediated proteins in forage fish native to the CF (inland silversides, *Menidia beryllina*) at environmental concentrations (Brander et al. 2012). This is of particular concern for migratory fishes in the CF considering the large quantity of CAFO waste water, agricultural run-off, treated wastewater effluent, and stormwater run-off discharged (Wing 2002; Mallin 2003; Costanza 2008). A study by Dwyer et al. (2000) investigated sensitivities of American shad, Atlantic and shortnose sturgeon to two POPs (4-nonyphenol, and pentachlorophenol), the pesticide permethrin (EDC), and copper (heavy metal). LC_{50} values were calculated for both species of sturgeon; however, American shad exhibited 62-70% mortality in control treatments and thus were left out of the results. This high mortality is indicative of the fragility and extreme sensitivity of American shad to such exposures. Atlantic and shortnose sturgeon had LC_{50} values for copper, 4-nonylphenol, pentachlorophenol, and permethrin as follows: $60 \mu\text{g l}^{-1}$ and $80 \mu\text{g l}^{-1}$; $50 \mu\text{g l}^{-1}$ and $80 \mu\text{g l}^{-1}$; $<40 \mu\text{g l}^{-1}$ and $70 \mu\text{g l}^{-1}$; and $<1.2 \mu\text{g l}^{-1}$ and $<1.2 \mu\text{g l}^{-1}$, respectively. Reported values show the sensitivity to low concentrations of contaminants in migratory fish such as those mentioned above.

Heavy metals such as arsenic (As) and mercury (Hg) also pose a threat to both fish and human health due to their ability to biomagnify, become more concentrated as they move up the food chain (Mallin et al. 2011). Tissue samples from bowfin, *Amia calva*, in the CF revealed levels unsafe for human consumption for As, cadmium (Cd), selenium (Se), and Hg. These concentrations cause a multitude of health impacts on fish including reproductive complications, kidney and liver failure, and deformities (Mallin 2011).

Plastic debris has been recognized as impacting aquatic ecosystems much longer than some of the more advanced toxicological approaches being implemented today, and yet

it is still one of the most prevalent forms of habitat degradation. Viehman et al. (2011) recently conducted a survey of NC saltmarshes that determined sites with the highest debris quantities were adjacent to concentrated coastal population centers, storm water discharges, and areas of concentrated marine use (boat launches, marinas, Intracoastal Waterway). The study observed small foam and plastic pieces (0-5 cm) were most common. Plastic debris was present in every site surveyed (n=15). The small plastic debris items are multifaceted hazards capable of environmental sorption of priority pollutants (POPs, EDCs, and metals) (Rochman 2013, 2014). These debris items absorb contaminants and harmful substances that are ingested and accumulate in fishes. Physical disruption of fish digestive systems coupled with harmful chemical delivery make plastic debris a multiple stressor in need of careful review. An emphasis on plastic debris education needs to be addressed to users of riverine and marine parks.

Climate Change and Anthropogenic Influences

Climate change and its impacts on water availability will inevitably complicate the situation in the CF. Historically habitat loss and over-exploitation of key species were the main human impacts on freshwater aquatic ecosystems. Over the last century those impacts have grown to include pollution, invasive species, and climate change (Crain et al. 2008). Increasing global temperatures coupled with nutrient enrichment of waterways will promote new extremes of algal growth, allowing the heat tolerant cyanobacteria spp. to outcompete other algae such as diatoms and chlorophytes (Paerl 2010). According to El-Shehawey (2012), not only will biomass of cyanobacteria increase, but a synergy between eutrophication and increasing temperatures will promote increased production of hepatotoxins. This increased production of toxins gives a competitive advantage and increased population fitness for local populations of cyanobacteria. It is important to consider multiple environmental factors to improve predictions of organismal responses to global environmental changes (Todgham 2013).

Frequency of flood and drought events will also increase. With drought there will be declines in dissolved oxygen content in lakes and streams contributing to anoxic

outbreaks and fish mortalities (Lake 2011). Increased evaporation of CAFO lagoons during drought events will increase deposition of nitrogen emissions increasing nitrogen inputs to coastal communities. Lack of rainfall may not be the only factor contributing to decreased water availability in the future. As human populations increase so does the demand on the water supply, bringing the water table lower. Falkenmark water stress indices incorporate supply (available water) and demand (population growth) for evaluating climate change induced water stress. Methods of water stress assessment will be important during periods of water limitation. Griffin et al. (2013) suggest that climate change has a significant impact on water resources but population growth has the most substantial impact.

As water levels drop due to elongated periods of drought or excessive water consumption by human populations, concentrations of toxins and harmful chemicals will increase and thrive in areas of low flow (Lake 2011). Excessive rainfall following a period of drought could then transport pockets of highly concentrated toxins and nutrients down the main stem of the Cape Fear exerting limitless destructive potential on the biota. According to a study outlining the impacts of flooding from Hurricane Floyd, flood waters may expose humans to contaminants from municipal solid waste facilities, sewage treatment facilities, hazardous waste facilities, and underground storage tanks containing petroleum products (Wing et al. 2002). A suggestion from Paerl (2010) is that in order to better prepare for future scenarios we require more complex water quality, eutrophication, and habitat models.

Necessary improvements to land use practices and conservation efforts are paramount. These changes are critical for improving water quality, fish passage and river flow and will only be possible through increased awareness, better education, and establishment of early indicators of toxic bloom events (El-Shehawey 2012). According to Mallin et al. (2006), impeded river flow resulting from the three LD structures in the CF reduced the washout rate (time of transport down the river system). This study attributes low water flow to phytoplankton bloom development behind the LD structures, which in turn

caused increased biochemical oxygen demand (BOD) due to downstream decomposition of algal cells. In addition to increased BOD, Burdick and Hightower (2006) observed that American shad and striped bass preferred higher water velocities to promote successful migration up the river, suggesting that these species will suffer from periods of drought or decreased river flow. Kennedy et al. (2008) compared the mean daily flow during a one-year study period (2006-2007) and found that flow averaged $97 \text{ m}^3\text{s}^{-1}$. Mean daily flow for the sampling period was 70% lower than the thirty-year average ($162\text{m}^3\text{s}^{-1}$), suggesting a dry year. Utilizing stress indices such as Falkenmark will help us anticipate and plan for potential water deficits that lie ahead.

Future Directions

From a conservation perspective, understanding the physiological capacity of sensitive organisms to cope with altered chemical regimes is paramount for the development of successful conservation and restoration strategies (Komoroske 2014). In other words, understanding the chemistry of the CF and how it affects the aquatic food web will help to establish effective FMPs. The NCDMF, NCDENR, and TNC are several groups that are analyzing data sets and creating programs to deal with water quality issues, improve fish stocks, and ensure the recreational and commercial use of the CF for future generations.

There are several nonprofit groups in existence that serve to educate the public and work to improve the conditions in the CF. One such group is the Cape Fear River Watch (CFRW), established in 1993 and committed to the improvement and preservation of the health, beauty, cleanliness, and heritage of the Cape Fear River Basin (capefearriverwatch.org). The CFRW offers environmental education and eco-tours that promote knowledge and awareness of the river and its fisheries. The WaterKeeper Alliance is a “neighborhood watch” program designed to protect communities and the waters on which they depend by making all waterways fishable, swimmable, and drinkable. The Lower Cape Fear River Program (LCFRP) and Cape Fear River Assembly (CFRA) are collaborations of government, industry, academia, and the public in the lower and middle reaches of the Cape Fear River basin who rely on the resources of the

river. Created in 1974 and 1995, respectively, the CFRA and LCFRP provide water quality monitoring and lead projects to improve water use and water quality management to ensure the health of the river system (<http://uncw.edu/cms/aelab/LCFRP/> and cfra-nc.org/). Nonprofit organizations, in collaboration with local and state government agencies are making great strides towards restoring healthy fish stocks and improving the water quality of the CF, but there is still significant work that needs to be done.

This study has identified a number of stressors affecting the aquatic communities of the CF and the quality of water that comprises the river. Irrigation water, for example, does not undergo the same criteria for water quality as our drinking water. This allows for fields of agriculture to be sprayed or irrigated with waters that may contain MCs (Codd 2000). In the case of CAFOs, they often spray waste lagoon water on fields, which then can allow bacterial coliform, MCs, pharmaceuticals, and numerous other contaminants to enter waterways via ground infiltration and storm water runoff (Mallin 2003), then entering important fish habitat. The importance of multiple stressor considerations when evaluating issues like eutrophication, persistence of algal blooms, input of persistent pollutants, and climate change, is critical. Crain et al. (2008) suggests that synergies are quite common in nature, implying that there is never just one culprit behind an environmental concern. A particular synergy to consider is eutrophication and climate change. According to El-Shehawy et al. (2012), increased temperatures promote growth and toxin production in cyanobacteria. Increased temperatures can also result in lower dissolved oxygen (DO) content in bodies of water, decreasing the amount of oxygen available to fish and other aquatic inhabitants. Inputs from nonpoint and point sources, aquatic debris and pollution, climate change, and occurrences of HABs are all challenges that will have to be dealt with by the organizations listed above in collaboration with the communities of the CF. Restoration of migratory routes and improved fish health are only possible through direct human intervention such as improving fish passages at LD structures and continued conservation efforts through effective fisheries management. Only then will we be able to reclaim and protect the

CF's biodiversity by ensuring the improvement and preservation of its water quality and ecological systems.

Future Avenues of Research

Significant gaps in available literature pertaining to toxicity of MCs and ammonia, nitrite and nitrate and their effects on fish health were identified by this review. Laboratory investigations involving exposure of larval and juvenile striped bass (*Morone saxatilis*) or the inland silver side (*Menidia beryllina*) to environmentally relevant concentrations of these toxins would be beneficial for understanding their impacts on fish health. Striped bass are less indicative of a particular region due to their large range of migration making the inland silver side (with a relatively small range) ideal for an indicator species. Experiments conducted in the lab could then be used to evaluate field samples that are collected during bloom events or periods of heavy nutrient loading. Laboratory results combined with field sampling will establish a better understanding of the impact of MCs, nitrates and nitrites on fish health and economically important fish stocks.

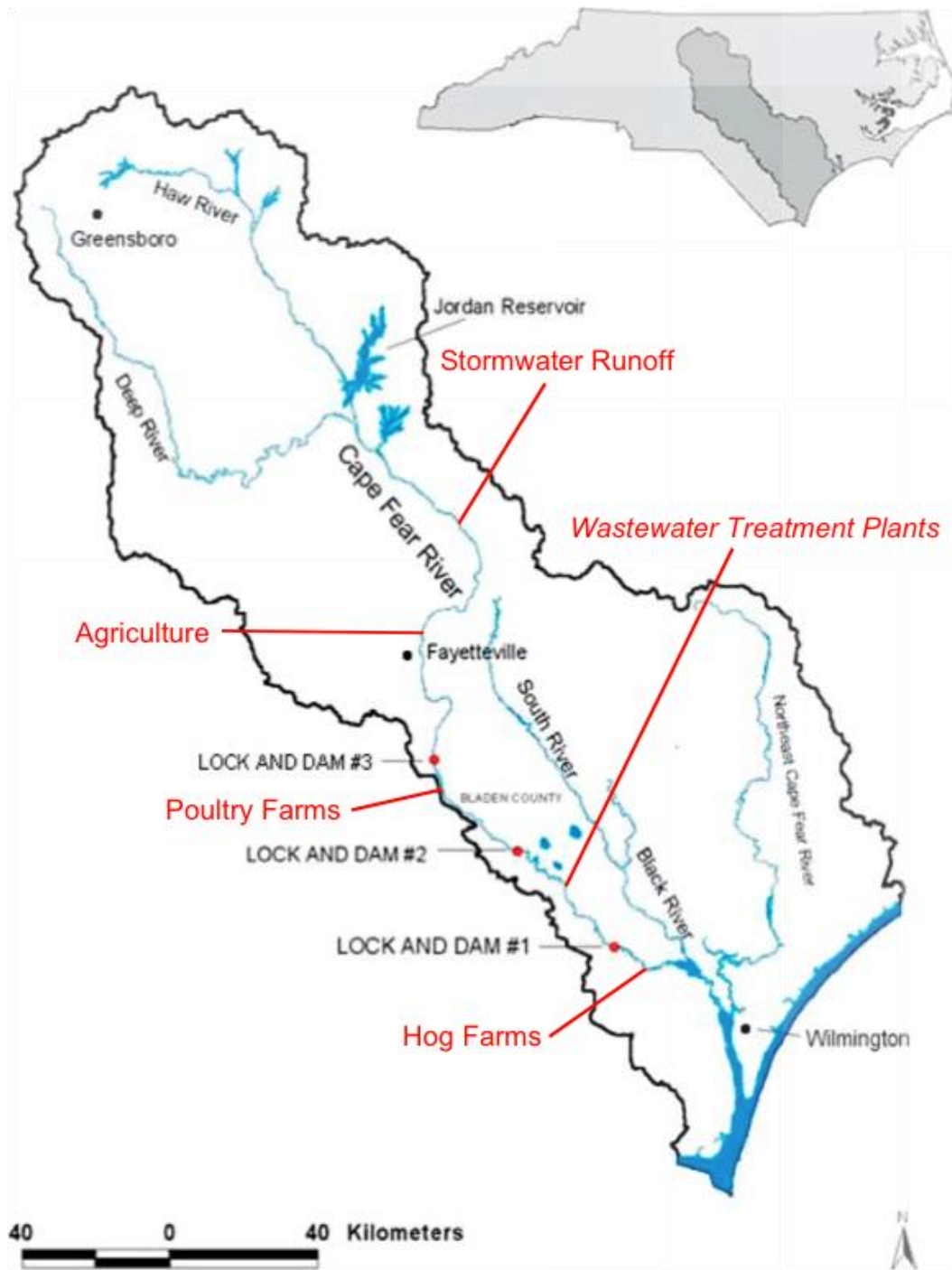
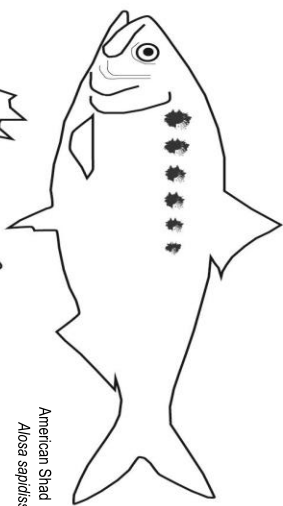


Figure 1. Cape Fear River Basin. LD structures 1,2, and 3 are designated, as are known point and non-point sources of nutrients and other pollutants (adapted from Dubbs et al. 2008).

MCS

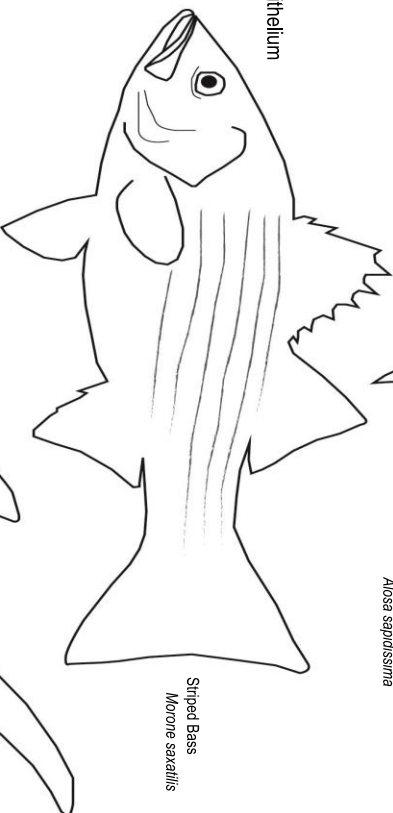
- accumulation of MCS in flesh and tissue (consumption risk)
- hepatocyte atrophy
- gill necrosis and respiratory complications
- endocrine disrupting effects
- epithelial ballooning, folded lamellar tips, exfoliation of lamellar epithelium
- difficulties maintaining anion/cation homeostasis
- genetic mutations



American Shad
Alosa sapidissima

Ammonia, Nitrate, Nitrite

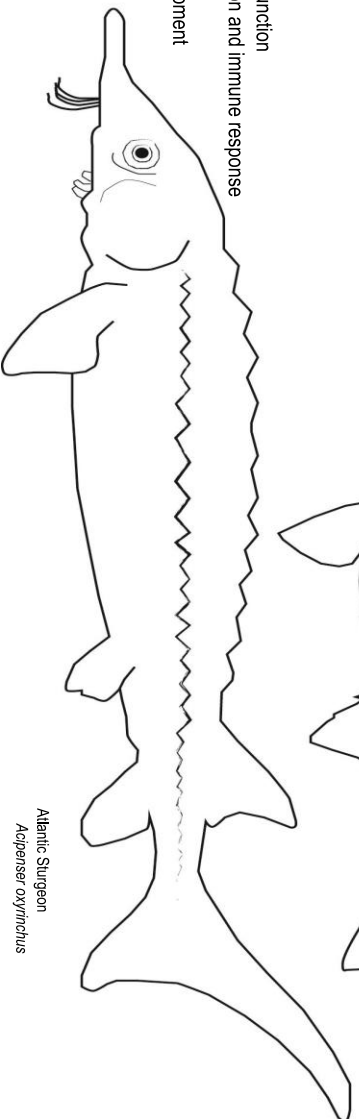
- suffocation through damage to gill epithelium
- elevated blood ammonia levels
- imbalances in osmoregulation
- decreased antibody production
- decreased growth rate
- methemoglobinemia
- disruption to chemosensory cues



Striped Bass
Morone saxatilis

EDCs

- altered hormone levels and function
- reduced mitochondrial function and immune response
- altered sex ratios
- interference to gonad development
- reduced fecundity



Atlantic Sturgeon
Acipenser oxyrinchus

Figure 2. Toxicological Impacts of Altered Water Quality on Migratory Fishes. A summary of effects resulting from exposure to microcystins, ammonia, nitrate, nitrite, and endocrine disrupting compounds on migratory fish species native to the Cape Fear.

Works Cited

- Bales, J. D., Oblinger, C. J., Sallenger A H., 2000. Two Months of Flooding in Eastern North Carolina, September–October 1999, Hydrologic, Water-Quality, and Geologic Effects of Hurricanes Dennis, Floyd, and Irene (USGS, Raleigh, NC) , USGS Water-Resources Investigations Report 00-4093.
- Brander, S. M., Cole, B. J., & Cherr, G. N., 2012. An approach to detecting estrogenic endocrine disruption via choriogenin expression in an estuarine model fish species. *Ecotoxicology*, 21(4), 1272-1280.
- Brander, S.M., 2013. Thinking outside the box: Assessing endocrine disruption in aquatic life, in: Ajuha, S. (Ed.), *Monitoring water quality: Pollution assessment, analysis, and remediation*. Elsevier, pp. 103-147.
- Burdick, S. M., & Hightower, J. E., 2006. Distribution of spawning activity by anadromous fishes in an Atlantic slope drainage after removal of a low-head dam. *Transactions of the American Fisheries Society* 135, (5), 1290-1300.
- Camargo, J. A., & Alonso, Á., 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. *Environment international*, 32(6), 831-849.
- Carbis, C. R., Rawlin, G. T., Grant, P., Mitchell, G. F., Anderson, J. W., & McCauley, I., 1997. A study of feral carp, *Cyprinus carpio* L., exposed to *Microcystis aeruginosa* at Lake Mokoan, Australia, and possible implications for fish health. *Journal of Fish Diseases*, 20(2), 81-91.
- Chorus, I., & Bartram, J., 1999. Toxic Cyanobacteria in Water. Retrieved July 15, 2014, from http://www.who.int/water_sanitation_health/resourcesquality/toxcyanobacteria.pdf?ua=1
- Codd, G. A., 2000. Cyanobacterial toxins, the perception of water quality, and the prioritisation of eutrophication control. *Ecological engineering*, 16(1), 51-60.
- Costanza, J. K., Marcinko, S. E., Goewert, A. E., & Mitchell, C. E., 2008. Potential geographic distribution of atmospheric nitrogen deposition from intensive livestock production in North Carolina, USA. *Science of the total environment* 398, (1), 76-86.
- Crain, C. M., Kroeker, K., & Halpern, B. S., 2008. Interactive and cumulative effects of multiple human stressors in marine systems. *Ecology letters*, 11(12), 1304-1315.
- de Figueiredo, D. R., Azeiteiro, U. M., Esteves, S. M., Gonçalves, F. J., & Pereira, M. J., 2004. Microcystin-producing blooms—a serious global public health issue. *Ecotoxicology and Environmental Safety*, 59(2), 151-163.
- Dubbs, L. L., & Whalen, S. C., 2008. Light- Nutrient Influences on Biomass, Photosynthetic Potential and Composition of Suspended Algal Assemblages in the Middle Cape Fear River, USA. *International Review of Hydrobiology*, 93(6), 711-730.
- Dwyer, F. J., Mayer, F. L., Sappington, L. C., Buckler, D. R., Bridges, C. M., Greer, I. E., ... & Neuderfer, G. N., 2005. Assessing contaminant sensitivity of endangered and threatened aquatic species: Part I. Acute toxicity of five chemicals. *Archives of environmental contamination and toxicology*, 48(2), 143-154.
- Eddy, F. B., 2005. Ammonia in estuaries and effects on fish. *Journal of Fish Biology*, 67(6), 1495-1513.

- Ensign, S. H., McMillan, S. K., Thompson, S. P., & Piehler, M. F., 2006. Nitrogen and phosphorus attenuation within the stream network of a coastal, agricultural watershed. *Journal of environmental quality* 35, (4), 1237-1247.
- El-Shehawy, R., Gorokhova, E., Fernandez-Pinas, F., & del Campo, F. F., 2012. Global warming and hepatotoxin production by cyanobacteria: What can we learn from experiments?. *water research*, 46(5), 1420-1429.
- Foster, N. R., 1985. Lake trout reproductive behavior: influence of chemosensory cues from young-of-the-year by-products. *Transactions of the American Fisheries Society*, 114(6), 794-803.
- Freitas de Magalhães, V., Moraes Soares, R., & Azevedo, S. M., 2001. Microcystin contamination in fish from the Jacarepaguá Lagoon (Rio de Janeiro, Brazil): ecological implication and human health risk. *Toxicon*, 39(7), 1077-1085.
- Gajdek, P., Lechowski, Z., Bochnia, T., Kepczynski, M., 2001. Decomposition of microcystin-LR by Fenton oxidation. *Toxicon* 39, 1575–1578.
- Griffin, M. T., Montz, B. E., & S Arrigo, J., 2013. Evaluating climate change induced water stress: A case study of the Lower Cape Fear basin, NC. *Applied Geography* 40, 115-128.
- Heisler, J., Glibert, P. M., Burkholder, J. M., Anderson, D. M., Cochlan, W., Dennison, W. C., ... & Suddleson, M., 2008. Eutrophication and harmful algal blooms: a scientific consensus. *Harmful algae* 8, (1), 3-13.
- Hines, D. E., Lisa, J. A., Song, B., Tobias, C. R., & Borrett, S. R., 2012. A network model shows the importance of coupled processes in the microbial N cycle in the Cape Fear River estuary. *Estuarine, Coastal and Shelf Science*, 106, 45-57.
- Hitzfeld, B. C., Höger, S. J., & Dietrich, D. R., 2000. Cyanobacterial toxins: removal during drinking water treatment, and human risk assessment. *Environmental health perspectives*, 108, Suppl 1, 113.
- Hrubec, T. C., Smith, S. A., & Robertson, J. L., 1996. Nitrate toxicity: a potential problem of recirculating systems. In *Proceedings from Successes and Failures in Commercial Recirculating Aquaculture Conference*, 41-48.
- Isaacs, J. D., Strangman, W. K., Barbera, A. E., Mallin, M. A., McIver, M. R., & Wright, J. L., 2014. Microcystins and two new micropeptin cyanopeptides produced by unprecedented *Microcystis aeruginosa* blooms in North Carolina's Cape Fear River. *Harmful Algae* 31, 82-86.
- Jang, M. H., Ha, K., Lucas, M. C., Joo, G. J., & Takamura, N., 2004. Changes in microcystin production by *Microcystis aeruginosa* exposed to phytoplanktivorous and omnivorous fish. *Aquatic Toxicology*, 68(1), 51-59.
- Jang, M. H., Ha, K., & Takamura, N., 2007. Reciprocal allelopathic responses between toxic cyanobacteria (*Microcystis aeruginosa*) and duckweed (*Lemna japonica*). *Toxicon*, 49(5), 727-733.
- Keefer, M. L., Caudill, C. C., Peery, C. A., & Moser, M. L., 2013. Context-dependent diel behavior of upstream-migrating anadromous fishes. *Environmental biology of fishes*, 96(6), 691-700.
- Kennedy, J. T., & Whalen, S. C., 2008. Seasonality and controls of phytoplankton productivity in the middle Cape Fear River, USA. *Hydrobiologia*, 598(1), 203-217.

- Komoroske, L. M., Connon, R. E., Lindberg, J., Cheng, B. S., Castillo, G., Hasenbein, M., & Fanguie, N. A., 2014. Ontogeny influences sensitivity to climate change stressors in an endangered fish. *Conservation Physiology*, 2(1), cou008.
- Lake, P. S., 2011. *Drought and aquatic ecosystems: effects and responses*. John Wiley & Sons.
- Lintelmann, J., Katayama, A., Kurihara, N., Shore, L., Wenzel, A., 2003. Endocrine disruptors in the environment (IUPAC Technical Report). *Pure and Applied Chemistry* 75, (5), 631-681.
- Mallin, M.A., Cahoon, L.B., 2003. Industrialized Animal Production—A Major Source of Nutrient and Microbial Pollution to Aquatic Ecosystems. *Population and Environment* 24, 369-385.
- Mallin, M. A., Johnson, V. L., & Ensign, S. H., 2009. Comparative impacts of stormwater runoff on water quality of an urban, a suburban, and a rural stream. *Environmental Monitoring and Assessment* 159, (1-4), 475-491.
- Mallin, M. A., McIver, M. R., Fulton, M., & Wirth, E., 2011. Elevated levels of metals and organic pollutants in fish and clams in the Cape Fear River watershed. *Archives of environmental contamination and toxicology*, 61(3), 461-471.
- Mallin, M. A. Personal Communication. 28 July 2014.
- Moore, A., Waring, C.P., 2001. The effects of a synthetic pyrethroid pesticide on some aspects of reproduction in Atlantic salmon (*Salmo salar* L.). *Aquatic Toxicology* 52, 1-12.
- Nakayama, S., Strynar, M.J., Helfant, L., Egeghy, P., Ye, X., Lindstrom, A.B., 2007. Perfluorinated Compounds in the Cape Fear Drainage Basin in North Carolina. *Environmental Science & Technology* 41, 5271-5276.
- Oppenborn, J. B., & Goudie, C. A., 1993. Acute and sublethal effects of ammonia on striped bass and hybrid striped bass. *Journal of the World Aquaculture Society*, 24(1), 90-101.
- Paerl, H. W., Rossignol, K. L., Hall, S. N., Peierls, B. L., & Wetz, M. S., 2010. Phytoplankton community indicators of short-and long-term ecological change in the anthropogenically and climatically impacted Neuse River Estuary, North Carolina, USA. *Estuaries and Coasts* 33, (2), 485-497.
- Peterson, B. J., Wollheim, W. M., Mulholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., ... & Morrall, D. D., 2001. Control of nitrogen export from watersheds by headwater streams. *Science*, 292(5514), 86-90.
- Ritter, L., Solomon, K. R., Forget, J., Stemmeroff, M., & O'leary, C., 1995. A review of selected persistent organic pollutants. International Programme on Chemical Safety (IPCS). PCS/95.39. Geneva: World Health Organization, 65, 66.
- Rochman, C. M., 2013. Plastics and priority pollutants: a multiple stressor in aquatic habitats. *Environmental science & technology*, 47(6), 2439-2440.
- Rochman, C. M., Hentschel, B. T., & Teh, S. J., 2014. Long-term sorption of metals is similar among plastic types: Implications for plastic debris in aquatic environments. *PloS one*, 9(1), e85433.
- Saul, B., 2014. Nutrient Associations with Cape Fear River Algal Blooms. The Nature Conservancy.
- Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., ... & Kasian, S. E. M., 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences*, 105(32), 11254-11258.

Smith, A., 2010. Prioritizing Cape Fear Arch Working Lands for Protection in Southeastern North Carolina. Doctoral dissertation, Duke University.

Todgham, A. E., & Stillman, J. H., 2013. Physiological responses to shifts in multiple environmental stressors: relevance in a changing world. *Integrative and comparative biology*, 53(4), 539-544.

Viehman, S., Vander Pluym, J.L., Schellinger, J., 2011. Characterization of marine debris in North Carolina salt marshes. *Marine Pollution Bulletin* 62, 2771-2779.

Vinodhini, R., & Narayanan, M., 2008. Bioaccumulation of heavy metals in organs of fresh water fish *Cyprinus carpio* (Common carp). *International Journal of Environmental Science & Technology*, 5(2), 179-182.

Wang, H., Zhong, G., Yan, H., Liu, H., Wang, Y., & Zhang, C., 2012. Growth Control of Cyanobacteria by Three Submerged Macrophytes. *Environmental engineering science* 29, (6), 420-425.

Webster, J. R., Mulholland, P. J., Tank, J. L., Valett, H. M., Dodds, W. K., Peterson, B. J., ... & Wollheim, W. M., 2003. Factors affecting ammonium uptake in streams—an inter- biome perspective. *Freshwater Biology*, 48(8), 1329-1352.

Wei, Y., Liu, Y., Wang, J., Tao, Y., & Dai, J., 2008. Toxicogenomic analysis of the hepatic effects of perfluorooctanoic acid on rare minnows, *Gobiocypris rarus*. *Toxicology and applied pharmacology*, 226(3), 285-297.

Williams, M. S. and Moser, M. L. 2000. Spawning of the Atlantic sturgeon (*Acipenser oxyrinchus*) in the Cape Fear River system, North Carolina. Report to the North Carolina Fisheries Resource Grant Program, North Carolina Sea Grant Program, Raleigh, NC.

Wing, S., Freedman, S., Band, L., 2002. The Potential Impact of Flooding on Confined Animal Feeding Operations in Eastern North Carolina. *Environmental Health Perspectives* 110, 387-391.

Yuan, B., Qu, J., Fu, M., 2002. Removal of cyanobacterial microcystin-LR by ferrate oxidation-coagulation. *Toxicon* 40 (8), 1129–1134.

Zhang, H., 2014. Temporal and Spatial Analysis of Water Quality and Landscape Characteristics for Albemarle Sound, North Carolina (Doctoral dissertation, Duke University).