Environmental Assessment of the Lower Cape Fear River System, 2012

By

Michael A. Mallin, Matthew R. McIver and James F. Merritt
October 2013

CMS Report No. 13-02
Center for Marine Science
University of North Carolina Wilmington
Wilmington, N.C. 28409

2.0 Physical, Chemical, and Biological Characteristics of the Lower Cape Fear River and Estuary

Michael A. Mallin and Matthew R. McIver
Aquatic Ecology Laboratory
Center for Marine Science
University of North Carolina Wilmington

2.1 - Introduction

This section of the report includes a discussion of the physical, chemical, and biological water quality parameters, concentrating on the January-December 2012 Lower Cape Fear River Program monitoring period. These parameters are interdependent and define the overall condition of the river. Physical parameters measured during this study included water temperature, dissolved oxygen, field turbidity and laboratory turbidity, total suspended solids (TSS), salinity, conductivity, pH and light attenuation. The chemical makeup of the Cape Fear River was investigated by measuring the magnitude and composition of nitrogen and phosphorus in the water. Three biological parameters including fecal coliform bacteria or enterococcus bacteria, chlorophyll *a* and biochemical oxygen demand were examined.

2.2 - Materials and Methods

All samples and field parameters collected for the estuarine stations of the Cape Fear River (NAV down through M18) were gathered on an ebb tide. This was done so that the data better represented the river water flowing downstream through the system rather than the tidal influx of coastal ocean water. Sample collection and analyses were conducted according to the procedures in the Lower Cape Fear River Program Quality Assurance/Quality Control (QA/QC) manual. Technical Representatives from the LCFRP Technical Committee and representatives from the NC Division of Water Quality inspect UNCW laboratory procedures and periodically accompany field teams to verify proper procedures are followed. Analysis methods are listed in Table 2.0.

<u>Physical Parameters</u>

Water Temperature, pH, Dissolved Oxygen, Turbidity, Salinity, Conductivity

Field parameters were measured at each site using a YSI 6920 (or 6820) multi-parameter water quality sonde displayed on a YSI 650 MDS. Each parameter is measured with individual probes on the sonde. At stations sampled by boat (see Table 1.1) physical parameters were measured at 0.1 m, the middle of the water column, and at the bottom (up to 12 m). Occasionally, high flow prohibited the sonde from reaching the actual bottom and measurements were taken as deep as possible. At the terrestrially sampled stations (i.e. from bridges or docks) the physical parameters were measured at a depth of 0.1 m.

The Aquatic Ecology Laboratory at the UNCW CMS is State-certified by the N.C. Division of Water Quality to perform field parameter measurements.

<u>Chemical Parameters</u>

Nutrients

A local State-certified analytical laboratory was contracted to conduct all chemical analyses except for orthophosphate, which is performed at CMS. The following methods detail the techniques used by CMS personnel for orthophosphate analysis.

Orthophosphate (PO_4^{-3})

Water samples were collected ca. 0.1 m below the surface in triplicate in amber 125 mL Nalgene plastic bottles and placed on ice. In the laboratory 50 mL of each triplicate was filtered through separate1.0 micron pre-combusted glass fiber filters, which were frozen and later analyzed for chlorophyll *a*. The triplicate filtrates were pooled in a glass flask, mixed thoroughly, and approximately 100 mL was poured into a 125 mL plastic bottle to be analyzed for orthophosphate. Samples were frozen until analysis.

Orthophosphate analyses were performed in duplicate using an approved US EPA method for the Bran-Lubbe AutoAnalyzer (Method 365.5). In this technique the orthophosphate in each sample reacts with ammonium molybdate and anitmony potassium tartrate in an acidic medium (sulfuric acid) to form an anitmony-phospho-molybdate complex. The complex is then reacted with ascorbic acid and forms a deep blue color. The intensity of the color is measured at a wavelength of 880 nm by a colorimeter and displayed on a chart recorder. Standards and spiked samples were analyzed for quality assurance.

<u>Biological Parameters</u>

Fecal Coliform Bacteria

Fecal coliform bacteria were analyzed by a State-certified laboratory contracted by the LCFRP. Samples were collected approximately 0.1 m below the surface in sterile plastic bottles provided by the contract laboratory and placed on ice for no more than six hours before analysis. After August 2011 the fecal coliform analysis was changed to *Enterococcus* in the estuarine stations downstream of NAV and HB (Stations BRR, M61, M35, M23 and M18).

Chlorophyll a

The analytical method used to measure chlorophyll *a* is described in Welschmeyer (1994) and US EPA (1997) and was performed by CMS personnel. Chlorophyll *a* concentrations were determined utilizing the 1.0 micron filters used for filtering samples for orthophosphate analysis. All filters were wrapped individually in foil, placed in airtight containers and stored in the freezer. During analysis each filter was immersed in 10 mL of

90% acetone for 24 hours, which extracts the chlorophyll *a* into solution. Chlorophyll *a* concentration of each solution was measured on a Turner 10-AU fluorometer. The fluorometer uses an optimal combination of excitation and emission bandwidth filters which reduces the errors inherent in the acidification technique. The Aquatic Ecology Laboratory at the CMS is State-certified by the N.C. Division of Water Quality for the analysis of chlorophyll *a*.

Biochemical Oxygen Demand (BOD)

Five sites were originally chosen for BOD analysis. One site was located at NC11, upstream of International Paper, and a second site was at AC, about 3 miles downstream of International Paper (Fig.1.1). Two sites were located in blackwater rivers (NCF117 and B210) and one site (BBT) was situated in an area influenced by both the mainstem Cape Fear River and the Black River. For the sampling period May 2000-April 2004 additional BOD data were collected at stream stations 6RC, LCO, GCO, BRN, HAM and COL in the Cape Fear and Black River watersheds. In May 2004 those stations were dropped and sampling commenced at ANC, SAR, GS, N403, ROC and BC117 in the Northeast Cape Fear River watershed for several years. The procedure used for BOD analysis is Method 5210 in Standard Methods (APHA 1995). Samples were analyzed for both 5-day and 20-day BOD. During the analytical period, samples were kept in airtight bottles and placed in an incubator at 20^{o} C. All experiments were initiated within 6 hours of sample collection. Samples were analyzed in duplicate. Dissolved oxygen measurements were made using a YSI Model 5000 meter that was air-calibrated. No adjustments were made for pH since most samples exhibited pH values within or very close to the desired 6.5-7.5 range (pH is monitored during the analysis as well); a few sites have naturally low pH and there was no adjustment for these samples because it would alter the natural water chemistry and affect true BOD. Data are presented within for the five original sites.

2.3 - Results and Discussion

This section includes results from monitoring of the physical, biological, and chemical parameters at all stations for the time period January-December 2012. Discussion of the data focuses both on the river channel stations and stream stations, which sometimes reflect poorer water quality than mainstem stations. The contributions of the two large blackwater tributaries, the Northeast Cape Fear River and the Black River, are represented by conditions at NCF117 and B210, respectively. The Cape Fear Region did not experience any significant hurricane activity during this monitoring period (after major hurricanes in 1996, 1998, and 1999). Therefore this report reflects low to medium flow conditions for the Cape Fear River and Estuary.

Physical Parameters

Water temperature

Water temperatures at all stations ranged from 3.3 to 32.1^{o}C, and individual station annual averages ranged from 15.9 to 20.9^{o}C (Table 2.1). Highest temperatures occurred during July and August and lowest temperatures during January. Stream stations were generally cooler than river stations, most likely because of shading and lower nighttime air temperatures affecting the shallower waters.

Salinity

Salinity at the estuarine stations (NAV through M18; also NCF6 in the Northeast Cape Fear River) ranged from 0.1 to 35.1 practical salinity units (psu) and station annual means ranged from 3.1 to 31.0 psu (Table 2.2). Lowest salinities occurred in spring and also in September and highest salinities occurred in winter. The annual mean salinity for 2012 was higher than that of the fifteen-year average for 1995-2011 for all of the estuarine stations (Figure 2.1), due to reduced river flows. Two stream stations, NC403 and PB, had occasional oligohaline conditions due to discharges from pickle production facilities. SC-CH is a tidal creek that enters the Northeast Cape Fear River upstream of Wilmington and salinity there ranged widely, from 0.4 to 10.2 psu.

Conductivity

Conductivity at the estuarine stations ranged from 0.14 to 53.3 mS/cm and from 0.07 to 5.50 mS/cm at the freshwater stations (Table 2.3). Temporal conductivity patterns followed those of salinity. Dissolved ionic compounds increase the conductance of water, therefore, conductance increases and decreases with salinity, often reflecting river flow conditions due to rainfall. Stations PB and NC403 are below industrial discharges, and often have elevated conductivity. Smith Creek (SC-CH) is an estuarine tidal creek and the conductivity values reflect this (Table 2.3).

pH

pH values ranged from 3.3 to 8.1 and station annual means ranged from 3.7 to 8.0 (Table 2.4). pH was typically lowest upstream due to acidic swamp water inputs and highest downstream as alkaline seawater mixes with the river water. Low pH values at COL predominate because of naturally acidic blackwater inputs at this near-pristine stream station. We also note that LRC had an unusually high pH level (7.8) in May 2012 (Table 2.3).

Dissolved Oxygen

Dissolved oxygen (DO) problems have been a major water quality concern in the lower Cape Fear River and its estuary, and several of the tributary streams (Mallin et al. 1999; 2000; 2001a; 2001b; 2002a; 2002b; 2003; 2004; 2005a; 2006a; 2006b; 2007; 2008; 2009;

2010; 2011; 2012). Surface concentrations for all sites in 2012 ranged from 0.3 to 12.6 mg/L and station annual means ranged from 3.0 to 9.4 mg/L (Table 2.5). Average annual DO levels at the river channel and estuarine stations for 2012 were slightly lower than the average for 1995-2011 (Figure 2.2). River dissolved oxygen levels were lowest during the summer and early fall (Table 2.5), often falling below the state standard of 5.0 mg/L at several river and upper estuary stations. Working synergistically to lower oxygen levels are two factors: lower oxygen carrying capacity in warmer water and increased bacterial respiration (or biochemical oxygen demand, BOD), due to higher temperatures in summer. Unlike other large North Carolina estuaries (the Neuse, Pamlico and New River) the Cape Fear estuary rarely suffers from dissolved oxygen stratification. This is because despite salinity stratification the oxygen remains well mixed due to strong estuarine gravitational circulation and high freshwater inputs (Lin et al. 2006). Thus, hypoxia in the Cape Fear is present throughout the water column.

There is a dissolved oxygen sag in the main river channel that begins at DP below a paper mill discharge and persists into the mesohaline portion of the estuary (Fig. 2.2). Mean oxygen levels were highest at the upper river stations NC11 and AC and in the low-to-middle estuary at stations M35 to M18. Lowest mainstem mean 2012 DO levels occurred at the river and upper estuary stations IC, NAV, HB, BRR and M61 (6.2-6.6 mg/L). HB, BRR, DP and M61 were all below 5.0 mg/L on 33% or more of occasions sampled, BBT was below on 25%, and NCF6 was below on 17% of occasions sampled, a deterioration from 2011. Based on number of occasions the river stations were below 5 mg/L UNCW rated HB, BRR, DP and M61 as poor for 2012; the mid to lower estuary stations were rated as good. Discharge of high BOD waste from the paper/pulp mill just above the AC station (Mallin et al. 2003), as well as inflow of blackwater from the Northeast Cape Fear and Black Rivers, helps to diminish oxygen in the lower river and upper estuary. Additionally, algal blooms periodically form behind Lock and Dam #1 (including the blue-green algal blooms in recent years), and the chlorophyll *a* they produce is strongly correlated with BOD at Station NC11 (Mallin et al. 2006b); thus the blooms do contribute to lower DO in the river. As the water reaches the lower estuary higher algal productivity, mixing and ocean dilution help alleviate oxygen problems.

The Northeast Cape Fear and Black Rivers generally have lower DO levels than the mainstem Cape Fear River (NCF117 2012 mean = 5.8, NCF6 = 6.3, B210 2012 mean = 6.5) . These rivers are classified as blackwater systems because of their tea colored water. As the water passes through swamps en route to the river channel, tannins from decaying vegetation leach into the water, resulting in the observed color. Decaying vegetation on the swamp floor has an elevated biochemical oxygen demand and usurps oxygen from the water, leading to naturally low dissolved oxygen levels. Runoff from concentrated animal feeding operations (CAFOs) may also contribute to chronic low dissolved oxygen levels in these blackwater rivers (Mallin et al. 1998; 1999; 2006; Mallin 2000). We note that phosphorus and nitrogen (components of animal manure) levels have been positively correlated with BOD in the blackwater rivers and their major tributaries (Mallin et al. 2006b).

Several stream stations were severely stressed in terms of low dissolved oxygen during the year 2012. Stations BCRR and SR had DO levels below 4.0 mg/L 67% of the occasions sampled, with NC403 58%, BC117 50%, LVC2 42%, GS 33% and NCF117 and SC-CH 25% (Table 2.5). Some of this can be attributed to low summer water conditions and some potentially to CAFO runoff; however point-source discharges also likely contribute to low dissolved oxygen levels at NC403 and possibly SR, especially via nutrient loading (Mallin et al. 2001a; 2002a; 2004). Hypoxia is thus a continuing and widespread problem, with 47% of the sites impacted in 2012.

Field Turbidity

Field turbidity levels ranged from 0 to 50 Nephelometric turbidity units (NTU) and station annual means ranged from 1 to 20 NTU (Table 2.6). The State standard for estuarine turbidity is 25 NTU. Annual mean turbidity levels for 2012 were lower than the long-term average at all estuary sites (Fig. 2.3), due to reduced river flow. Highest mean turbidities were at NAV and HB (17-20 NTU) with turbidities generally low in the middle to lower estuary (Figure 2.3). Stations NAV, HB and BRR exceeded the estuarine turbidity standard on four, three and two occasions, respectively. Turbidity was considerably lower in the blackwater tributaries (Northeast Cape Fear River and Black River) than in the mainstem river. Average turbidity levels were low in the freshwater streams, with the exception of PB, SR and to a lesser extent LCO. The State standard for freshwater turbidity is 50 NTU.

Note: In addition to the laboratory-analyzed turbidity that are required my NCDWQ for seven locations, the LCFRP uses nephelometers designed for field use, which allows us to acquire in situ turbidity from a natural situation. North Carolina regulatory agencies are required to use turbidity values from water samples removed from the natural system, put on ice until arrival at a State-certified laboratory, and analyzed using laboratory nephelometers. Standard Methods notes that transport of samples and temperature change alters true turbidity readings. Our analysis of samples using both methods shows that lab turbidity is nearly always lower than field turbidity; thus we do not discuss lab turbidity in this report.

Total Suspended Solids

Total suspended solid (TSS) values system wide ranged from 1 to 51 mg/L with station annual means from 2 to 19 mg/L (Table 2.7). The overall highest river values were at NAV and M18. In the stream stations TSS was generally considerably lower than the river and estuary, except for a few incidents at Station PB and Station ROC. Although total suspended solids (TSS) and turbidity both quantify suspended material in the water column, they do not always go hand in hand. High TSS does not mean high turbidity and vice versa. This anomaly may be explained by the fact that fine clay particles are effective at dispersing light and causing high turbidity readings, while not resulting in high TSS. On the other hand, large organic or inorganic particles may be less effective at dispersing light, yet their greater mass results in high TSS levels. While there is no NC ambient standard for TSS, many years of data from the lower Cape Fear watershed indicates that

25 mg/L can be considered elevated. The fine silt and clay in the upper to middle estuary sediments are most likely derived from the Piedmont and carried downstream to the estuary, while the sediments in the lowest portion of the estuary are marine-derived sands (Benedetti et al. 2006).

Light Attenuation

The attenuation of solar irradiance through the water column is measured by a logarithmic function (k) per meter. The higher this light attenuation coefficient is the more strongly light is attenuated (through absorbance or reflection) in the water column. River and estuary light attenuation coefficients ranged from 0.77 to 6.08/m and station annual means ranged from 1.29 at M18 to 4.17 /m at NCF6 (Table 2.8). Elevated mean and median light attenuation occurred from AC downstream to IC; the estuary from NAV-M54 also had high attenuation (Table 2.8). In the Cape Fear system, light is attenuated by both turbidity and water color.

High light attenuation did not always coincide with high turbidity. Blackwater, though low in turbidity, will attenuate light through absorption of solar irradiance. At NCF6 and BBT, blackwater stations with moderate turbidity levels, light attenuation was high. Compared to other North Carolina estuaries the Cape Fear has high average light attenuation. The high average light attenuation is a major reason why phytoplankton production in the major rivers and the estuary of the LCFR is generally low. Whether caused by turbidity or water color this attenuation tends to limit light availability to the phytoplankton (Mallin et al. 1997; 1999; 2004; Dubbs and Whalen 2008).

<u>Chemical Parameters – Nutrients</u>

Total Nitrogen

Total nitrogen (TN) is calculated from TKN (see below) plus nitrate; it is not analyzed in the laboratory. TN ranged from 50 (detection limit) to 11,100 μg/L and station annual means ranged from 288 to 2,313 μg/L (Table 2.9). Mean total nitrogen in 2012 was less than the sixteen-year mean at the river and estuary stations (Figure 2.4). Previous research (Mallin et al. 1999) has shown a positive correlation between river flow and TN in the Cape Fear system. In the main river total nitrogen concentrations were highest between NC11 and DP, entering the system, then declined into the lower estuary, most likely reflecting uptake of nitrogen into the food chain through algal productivity and subsequent grazing by planktivores as well as through dilution and marsh denitrification. The highest median TN value at the stream stations was at ROC, with 1,305 μg/L; other elevated TN values were seen at BC117, ANC, GCO and 6RC.

Nitrate+Nitrite

Nitrate+nitrite (henceforth referred to as nitrate) is the main species of inorganic nitrogen in the Lower Cape Fear River. Concentrations system wide ranged from 10 (detection limit) to 11,100 μg/L and station annual means ranged from 27 to 1,671 μg/L (Table 2.10). The highest average riverine nitrate levels were at NC11 and AC (942 and 890 μg/L, respectively) indicating that much of this nutrient is imported from upstream. Moving downstream, nitrate levels decrease most likely as a result of uptake by primary producers, microbial denitrification in riparian marshes and tidal dilution. Despite this, the rapid flushing of the estuary (Ensign et al. 2004) permits sufficient nitrate to enter the coastal ocean in the plume and contribute to offshore productivity (Mallin et al. 2005b). Nitrate can limit phytoplankton production in the lower estuary in summer (Mallin et al. 1999). The blackwater rivers carried lower concentrations of nitrate compared to the mainstem Cape Fear stations; i.e. the Northeast Cape Fear River (NCF117 mean = 278 μg/L) and the Black River (B210 = 203 μg/L). Lowest river nitrate occurred during summer, along with lowest flows and lowest dissolved oxygen concentrations.

Several stream stations showed high levels of nitrate on occasion including BC117, ROC, 6RC, GCO, SAR, LVC2 and BRN. 6RC, ROC, GCO and SAR and 6RC primarily receive non-point agricultural or animal waste drainage. BC117 always showed very high nitrate levels. The Town of Burgaw wastewater plant, upstream of BC117, has no nitrate discharge limits. Over the past several years a considerable number of experiments have been carried out by UNCW researchers to assess the effects of nutrient additions to water collected from blackwater streams and rivers (i.e. the Black and Northeast Cape Fear Rivers, and Colly and Great Coharie Creeks). These experiments have collectively found that additions of nitrogen (as either nitrate, ammonium, or urea) significantly stimulate phytoplankton production and BOD increases. Critical levels of these nutrients were in the range of 0.2 to 0.5 mg/L as N (Mallin et al. 1998; Mallin et al. 2001a; Mallin et al. 2002a, Mallin et al. 2004). Thus, we conservatively consider nitrate concentrations exceeding 0.5 mg/L as N in Cape Fear watershed streams to be potentially problematic to the stream's environmental health.

Ammonium/ammonia

Ammonium concentrations ranged from 5 (detection limit) to 3,380 μg/L and station annual means ranged from 5 to 372 μg/L (Table 2.11). River areas with the highest mean ammonium levels this monitoring period included AC and DP, which are downstream of a pulp mill discharge, and M61, located just upstream of the Wilmington South Side Wastewater Treatment Plant discharge. Ocean dilution and biological uptake accounts for decreasing levels in the lower estuary. At the stream stations, areas with highest levels of ammonium were PB, LVC2, ANC, BC117, BCRR and ROC (Table 2.11). ANC had an unusually high peak concentration of 3,380 μg/L in July for unknown reasons.

Total Kjeldahl Nitrogen

Total Kjeldahl Nitrogen (TKN) is a measure of the total concentration of organic nitrogen plus ammonium. TKN ranged from 50 (detection limit) to 6,000 μg/L and station annual means ranged from 233 to 1,300 μg/L (Table 2.12). TKN concentration decreases ocean-ward through the estuary, likely due to ocean dilution and food chain uptake of nitrogen. One notably elevated peak of 6,000 μg/L of TKN was seen at ANC in July; ANC also had the highest median concentrations. Other sites with elevated TKN included ROC, GCO, SR and COL.

Total Phosphorus

Total phosphorus (TP) concentrations ranged from 10 (detection limit) to 1,400 μg/L and station annual means ranged from 32 to 432 μg/L (Table 2.13). Mean TP for 2012 was somewhat higher than the sixteen-year mean in the estuary and river stations (Figure 2.5). In the river TP is highest at the upper riverine channel stations NC11 and AC and declines downstream into the estuary. Some of this decline is attributable to the settling of phosphorus-bearing suspended sediments, yet incorporation of phosphorus into bacteria and algae is also responsible.

The experiments discussed above in the nitrate subsection also involved additions of phosphorus, either as inorganic orthophosphate or a combination of inorganic plus organic P. The experiments showed that additions of P exceeding 0.5 mg/L led to significant increases in bacterial counts, as well as significant increases in BOD over control. Thus, we consider concentrations of phosphorus above 0.5 mg/L (500 μg/L) to be potentially problematic to blackwater streams (Mallin et al. 1998; 2004). Streams periodically exceeding this critical concentration included BC117, GCO, ROC and NC403. Some of these stations (BC117, NC403) are downstream of industrial or wastewater discharges, while GCO and ROC are in non-point agricultural areas.

Orthophosphate

Orthophosphate ranged from undetectable to 1,180 μg/L and station annual means ranged from 6 to 328 μg/L (Table 2.14). Much of the orthophosphate load is imported into the Lower Cape Fear system from upstream areas, as NC11 or AC typically have high levels; there are also inputs of orthophosphate from the paper mill above AC (Table 2.14). The Northeast Cape Fear River had higher orthophosphate levels than the Black River. Orthophosphate can bind to suspended materials and is transported downstream via particle attachment; thus high levels of turbidity at the uppermost river stations may be an important factor in the high orthophosphate levels. Turbidity declines toward the lower estuary because of settling, and orthophosphate concentration also declines. In the estuary, primary productivity helps reduce orthophosphate concentrations by assimilation into biomass. Orthophosphate levels typically reach maximum concentrations during summertime, when anoxic sediment releases bound phosphorus. Also, in the Cape Fear Estuary, summer algal productivity is limited by nitrogen, thereby allowing the accumulation of orthophosphate (Mallin et al. 1997; 1999). In spring, productivity in the estuary is usually limited by phosphorus (Mallin et al. 1997; 1999).

The stream station BC117 had high orthophosphate levels, and ROC and GCO had comparatively high levels. BC117 is below a municipal wastewater discharge, and ROC and GCO are impacted by agriculture/animal waste runoff.

Chemical Parameters - EPA Priority Pollutant Metals

The LCFRP had previously sampled for water column metals (EPA Priority Pollutant Metals) on a bimonthly basis. However, as of 2007 this requirement was suspended by the NC Division of Water Quality and these data are no longer collected by the LCFRP.

Biological Parameters

Chlorophyll a

During this monitoring period in most locations chlorophyll *a* was low, except for elevated concentrations in July and August at the river and upper estuary stations (Table 2.15). The only exceedence of the state standard was for 54 µg/L at Station 61 in August; there was also a bloom or 40 µg/L at AC in July. We note that at the upper site NC11 it has been demonstrated that chlorophyll *a* biomass is significantly correlated with biochemical oxygen demand (BOD5 – Mallin et al. 2006b). What is of human health concern as well as ecological interest was that blooms of cyanobacteria (blue-green algae) called *Microcystis aeruginosa* began occurring in 2009 and continued to occur in summer 2010, 2011 and 2012. This species contains many strains long known to produce toxins, both as a threat to aquatic life and to humans as well (Burkholder 2002). At least some of the blooms in the main stem of the Cape Fear have produced toxins. The North Carolina Division of Public Health had a 2009 bloom sample from Lock and Dam #1 tested and it came out positive for 73 ppb (μg/L) of microcystin (Dr. Mina Shehee, NC Division of Public Health, memo September 25, 2011), resulting in an advisory to keep children and dogs from swimming in the waters. For comparison, the World Health Organization has a guideline of < 1.0 μg/L of microcystin-LR for drinking water. Additional algal bloom material from the Cape Fear River collected in September 2009 was analyzed by Dr. Paul Zimba at Texas A&M University-Corpus Christi, who found a water microcystin RR concentration of 391 µg/L. In related work UNCW researchers directed by chemists Dr. Jeff Wright and Dr. Wendy Strangman also isolated the two hepatotoxins, microcystin LR and microcystin RR, from Cape Fear *Microcystis aeruginosa* blooms in 2010 (Isaacs 2011). These researchers also found two new cyanopeptides, micropeptin 1106 and micropeptin 1120 in elevated concentrations; the biological activity of those two compounds is unknown. We note that the City of Wilmington and parts of Brunswick County receive their drinking water from the river above Lock and Dam #1 in the bloom area.

In 2012 a significant *Microcystis aeruginosa* bloom occurred in July in the vicinity of Lock and dam #1. Jared Metheny, a student under the direction of Dr. Mike Mallin found significant correlations between chlorophyll *a* and BOD5 in surface and sub-surface water at Stations NC11 and AC and downstream several miles. Dr. Larry Cahoon, of the UNCW Biology and Marine Biology Department, also collected a variety of chemical samples in association with blooms upstream of L&D#1, with the goal of gaining further understanding of how these blooms affect the river's ecology.

System wide, chlorophyll *a* ranged from undetectable to 54 μg/L and station annual means ranged from 2-8 μg/L, lower than in 2011. Production of chlorophyll *a* biomass is usually low to moderate in the rivers and estuary primarily because of light limitation by turbidity in the mainstem and high organic color and low inorganic nutrients in the blackwater rivers.

Spatially, besides Station NC11 along the mainstem high values are normally found in the mid-to-lower estuary stations because light becomes more available downstream of the estuarine turbidity maximum (Fig. 2.6). On average, flushing time of the Cape Fear estuary is rapid, ranging from 1-22 days with a median of 6.7 days (Ensign et al. 2004). This does not allow for much settling of suspended materials, leading to light limitation of phytoplankton production. However, under lower-than-average flows there is generally clearer water through less suspended material and less blackwater swamp inputs. For the growing season May-September, long-term (1995-2012) average monthly flow at Lock and Dam #1 was approximately 3,361 CFS (USGS data; (http://nc.water.usgs.gov/realtime/real_time_cape_fear.html), whereas for 2012 it was well below that at approximately 1,719 CFS. Thus, chlorophyll *a* concentrations in the river and estuary were mostly greater than the average for the preceding sixteen years (Figure 2.6).

Phytoplankton blooms occasionally occur at the stream stations, with a few occurring at various months in 2012 (Table 2.15). These streams are generally shallow, so vertical mixing does not carry phytoplankton cells down below the critical depth where respiration exceeds photosynthesis. Thus, when lower flow conditions prevail, elevated nutrient conditions (such as are periodically found in these stream stations) can lead to algal blooms. In areas where the forest canopy opens up large blooms can occur. When blooms occur in blackwater streams they can become sources of BOD upon death and decay, reducing further the low summer dissolved oxygen conditions common to these waters (Mallin et al. 2001a; 2002a; 2004; 2006b). Stations LRC, PB, NC403 and ANC all had minor algal blooms in 2012, although not exceeding the state standard of 40 µg/L (Table 2.15).

Biochemical Oxygen Demand

For the mainstem river, median annual five-day biochemical oxygen demand (BOD5) concentrations were approximately equivalent between NC11 and AC, suggesting that in 2012 (as was the case with 2007 through 2011) there was little discernable effect of BOD loading from the nearby pulp/paper mill inputs (Table 2.16). BOD5 values between 1.0 and 2.0 mg/L are typical for the rivers in the Cape Fear system (Mallin et al. 2006b) and in 2012 BOD5 values ranged from 0.3 – 4.2 mg/L. There were no major differences among sites for BOD5 or BOD20 in 2012. BOD20 values showed similar patterns to BOD5 in 2012.

Fecal Coliform Bacteria/ Enterococcus bacteria

Fecal coliform (FC) bacterial counts ranged from 1 to 60,000 CFU/100 mL and station annual geometric means ranged from 17 to 602 CFU/100 mL (Table 2.17). The state human contact standard (200 CFU/100 mL) was exceeded at the mainstem sites only once in 2012, at HB in September. During 2012 the stream stations showed high fecal coliform pollution levels. BC117 and HAM exceeded 200 CFU/100 mL 67% of the time;

BCRR and BRN 58%, PB and SAR 50%, GS, NC403, ROC, LROC SR and SC-CH 42%, ANC, GCO and LVC2 33% of the time. BC117, NC403 and PB are located below point source discharges and the other sites are primarily influenced by non-point source pollution.

Enterococcus counts were initiated in the estuary in mid-2011, as this test is now the standard used by North Carolina regulators for swimming in salt waters. Sites covered by this test include BRR, M61, M54, M35, M23 and M18. The State has a single-sample level for Tier II swimming areas in which the enterococci level in a Tier II swimming area shall not exceed a single sample of 276 enterococci per 100 milliliter of water (15A NCAC 18A .3402); the LCFRP is using this standard for the Cape Fear estuary samples in our rating system. As such, in 2012 most estuary sites exceeded the standard on two occasions, yielding a Fair rating by our standards. Overall, elevated fecal coliform and enterococcus counts are problematic in this system, with 66% of the stations rated as Fair or Poor in 2012, higher than the previous year 2011.

2.4 - References Cited

APHA. 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. American Public Health Association, Washington, D.C.

Benedetti, M.M., M.J. Raber, M.S. Smith and L.A. Leonard. 2006. Mineralogical indicators of alluvial sediment sources in the Cape Fear River basin, North Carolina. *Physical Geography* 27:258-281.

Burkholder. J.M. 2002. Cyanobacteria. *In* “Encyclopedia of Environmental Microbiology” (G. Bitton, Ed.), pp 952-982. Wiley Publishers, New York.

Dubbs, L. L. and S.C. Whalen. 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* 93:711-730.

Ensign, S.H., J.N. Halls and M.A. Mallin. 2004. Application of digital bathymetry data in an analysis of flushing times of two North Carolina estuaries. *Computers and Geosciences* 30:501-511.

Isaacs, J.D. 2011. Chemical investigations of the metabolites of two strains of toxic cyanobacteria. M.S. Thesis, University of North Carolina Wilmington, Wilmington, N.C.

Lin, J. L. Xie, L.J. Pietrafesa, J. Shen, M.A. Mallin and M.J. Durako. 2006. Dissolved oxygen stratification in two microtidal partially-mixed estuaries. *Estuarine, Coastal and Shelf Science.* 70:423-437.

Mallin, M.A. 2000. Impacts of industrial-scale swine and poultry production on rivers and estuaries. *American Scientist* 88:26-37.

Mallin, M.A., L.B. Cahoon, M.R. McIver, D.C. Parsons and G.C. Shank. 1997. Nutrient limitation and eutrophication potential in the Cape Fear and New River Estuaries.