



# Satellite remote sensing of chlorophyll *a* in support of nutrient management in the Neuse and Tar–Pamlico River (North Carolina) estuaries



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## ABSTRACT

The North Carolina Environmental Management Commission (EMC) has adopted as a water quality standard that chlorophyll *a* concentration should not exceed 40  $\mu\text{g/L}$  in sounds, estuaries and other slow-moving waters. In 1996, nutrient load reductions were placed into North Carolina (NC) law to reduce the extent and duration of algal blooms in the Neuse and Tar River estuaries (Session Law 1995, Section 572). The chlorophyll *a* criterion was used as the endpoint to manage total nitrogen concentrations, and compliance would be achieved if chl *a* exceedances occurred in fewer than 10% of the samples collected in a specified area and time (known as the 10/40 criterion).

In 2009, discussions were held between the North Carolina Department of Environmental and Natural Resources (NCDENR) and US Environmental Protection Agency (EPA) concerning the practicality of using satellite-derived chl *a* concentrations to monitor water quality, enforce water quality-related environmental regulations, and understand the environmental impacts of the watershed land-use practices on coastal waters.

In this study, the MERIS chlorophyll *a* data product was used to conduct a retrospective analysis of the NC standard for water quality and Total Maximum Daily Load (TMDL) for total nitrogen in the Neuse and Tar–Pamlico River estuaries from 2006 to 2009. From daily MERIS images, compliance and chlorophyll exceedances in the Neuse and Tar–Pamlico River estuaries were assessed at daily and aggregated to annual time scales.

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## 1. Introduction

The State of North Carolina Environmental Management Commission (EMC) has adopted as a water quality standard that chlorophyll *a* concentrations in sounds and estuaries should not exceed 40  $\mu\text{g/L}$  (NC Administrative Code Section 15A NCAC 2B.0212). The standard was based on research conducted in freshwater reservoirs by the University of North Carolina Water Resources Research Institute (WRRRI). However, the legislation did not include specifics on sampling methodology or, at that time, the definition of what constituted a violation (WRRRI, 2001). The standard was developed in response to nuisance algal blooms and eutrophic events in the lower Neuse River basin which occurred during the late 1970s, early 1980s and into the 1990s (Paerl, Mallin, Rudek, & Bates, 1990). Investigations by the North Carolina Division of Water Quality (NCDWQ) concluded that algal growth was being stimulated by excess nutrients (primarily nitrogen and phosphorus) caused by agricultural and urban expansion in watersheds upstream of the

estuaries (Dodd, Cunningham, Curry, & Stichter, 1993; NCDWQ, 2009; Stanley, 1988).

According to NC state law, once a water body surpassed this standard, regulators were to develop a Total Maximum Daily Load (TMDL) for nutrients in that water body (NCDWQ, 2009). To determine the appropriate TMDL for the Neuse River Estuary (NRE), NCDWQ used a phased approach involving development in two phases. The Phase I TMDL was developed from predictions of three water quality models on the expected frequency of exceeding the state chlorophyll standard in a specified period under a variety of nitrogen loading scenarios (Borsuk, Clemen, Maguire, & Reckhow, 2001; Borsuk, Stow, & Reckhow, 2003; NCDENR, 2001; Stow, Borsuk, & Stanley, 2001; Stow, Roessler, Borsuk, Bowen, & Reckow, 2003). For the Neuse River, the input level was established as a 30% reduction in nitrogen concentrations from the 1991 to 1995 baseline dataset in the Neuse River. This 30% reduction of the baseline load of 9.65 million pounds of TN per year equated to a TMDL of 6.75 million pounds per year (NCDENR, 2001). The TMDL is governed by the “10/40” criterion under which compliance is achieved when less than ten percent of samples collected in a specified area and time within the Neuse River Estuary exceed the state chl *a* water quality standard of 40  $\mu\text{g/L}$  (NCDENR, 2001).

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The Phase II TMDL goal was to achieve compliance of the 10/40 criterion through the development of a Nutrient Sensitive Waters (NWS) Management Strategy. Tools and data from the Neuse River Modeling and Monitoring Project (ModMon) were incorporated in the NSW strategy to evaluate the effectiveness of the TMDL in reducing the nitrogen load by 30% and determine if the chlorophyll *a* criterion was met (NCDENR, 2001). In 2002, the nitrogen TMDL was approved by EPA to address nitrogen overloading to the NRE.

In October 2009, an EPA-sponsored workshop was convened to discuss incorporating satellite-derived chlorophyll values into the NC State decision process and assess the potential of the European Space Agency (ESA) MERIS chlorophyll product becoming an integral component of future monitoring of the Albemarle–Pamlico estuarine system. Workshop participants agreed that the high temporal and spatial resolution of the MERIS chl *a* product could be beneficial during the development of water quality regulations based on “phytoplankton density” criteria. It was also agreed that the MERIS product could be used to support retrospective analysis for the development of new nutrient regulations and revisions of the current TMDL process, and to site future *in situ* monitoring locations and detect unknown bloom events. Participants recommended that the MERIS chl *a* product be considered in an operational mode to provide a long-term record of phytoplankton concentrations to support future regulation of nutrient loadings.

### 1.1. Neuse and Pamlico estuaries

The Neuse and Pamlico estuaries are part of the Albemarle–Pamlico Estuarine System (APES; Fig. 1) which is the second largest estuary in the Nation, measuring approximately 52,000 km<sup>2</sup> (31,000 miles<sup>2</sup>; APNEP). In addition to the Neuse and Pamlico, the APES includes the Albemarle, Pamlico Sounds (Fig. 1), as well as Roanoke, Chowan, and Alligator Rivers, and Currituck, Croatan, and Roanoke Sounds (not shown). Inflow to Pamlico Sound from the Pamlico River averages around 5400 ft<sup>3</sup> per second, and average inflow into the Neuse River

estuary is about 6100 ft<sup>3</sup> per second. Approximately one-half of the inflow into the system is from groundwater discharge (Harned & Davenport, 1990). The APES is protected by an extensive barrier island system with only a few small inlets connecting to the Atlantic Ocean (NCDENR, 1989) creating long water residence times and periodic strong vertical stratification of the water column. The APES subestuaries are shallow (average 1–3 m depth), microtidal, (<1 ft tidal range), oligohaline–mesohaline estuaries with water residence times that range from several weeks during high freshwater discharge periods in winter to several months during the summer (Wetz, Hutchinson, Lunetta, Paerl, & Taylor, 2011).

During the late 1970s through early 1990s, the Neuse and Pamlico River estuaries were impacted by several climatic (hurricanes, tropical storms) and hydrologic (high discharge periods) events which lead to increased loading of nitrate (NO<sub>3</sub>), dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), and phosphorus (dissolved inorganic phosphorus (DIP) and total phosphorus) into the NRE (Paerl, Rossignol, Hall, Peierls, & Wetz, 2010). The response to the increased DIN was excessive chlorophyll concentrations that led to eutrophication, fish kills, harmful algal blooms, hypoxia, and declines in water quality. The sources of excessive nutrients include runoff from row crops, confined animal feeding operations, and highly erodable soils ([http://water.epa.gov/polwaste/nps/success319/nc\\_tar.cfm](http://water.epa.gov/polwaste/nps/success319/nc_tar.cfm)).

The Neuse River Estuary (NRE) is the largest estuary in the Albemarle–Pamlico Estuarine System and is an extension of the Neuse River which is the longest river in North Carolina (Fig. 2; NCDWQ, 2009; Lunetta et al., 2009). NCDWQ defined five estuarine segments within the Neuse River estuary for periodic monitoring based on designated use and nutrient loading modeling (Fig. 2; Stow et al., 2003). Use classifications are categories assigned to all surface waters in North Carolina based on the best-intended use of those waters (NCDWQ, 2009). The segments were designated as the Neuse River segment, Upper Neuse River Estuary segment, Middle Neuse River Estuary segment, the Bend segment, and Lower Neuse River Estuary segment. Historically, the Upper Neuse River Estuary and Middle Neuse River

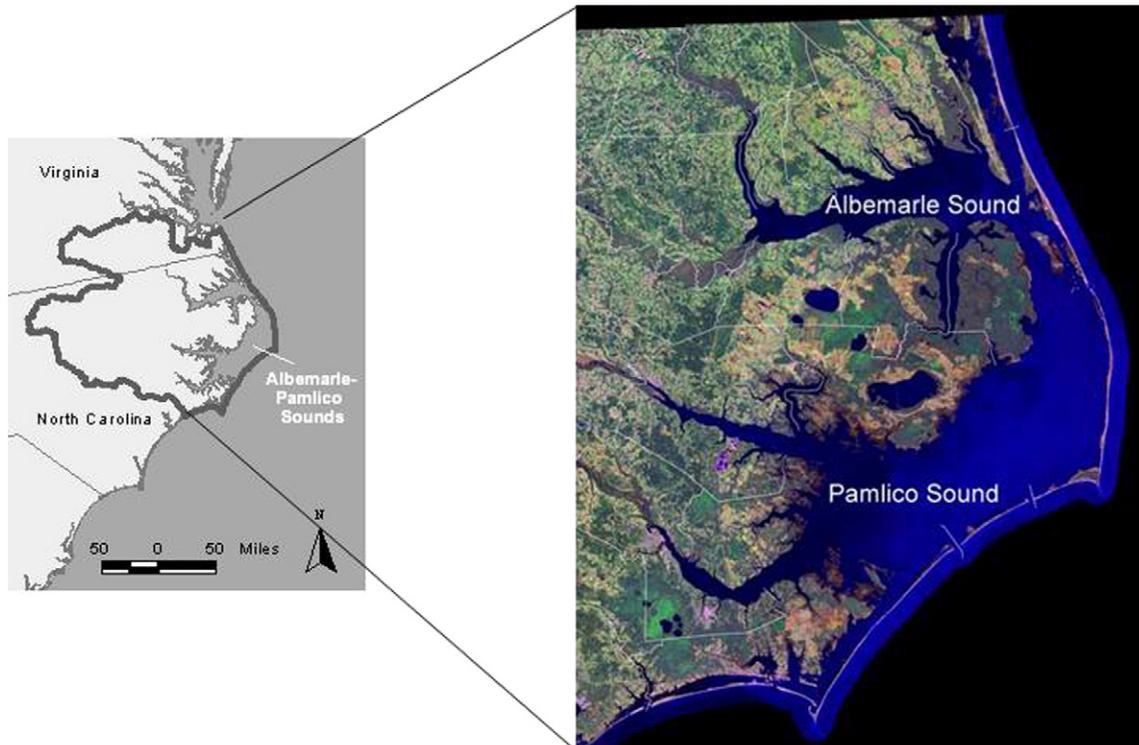


Fig. 1. The Albemarle–Pamlico Estuarine System (images courtesy of EPA and USGS).

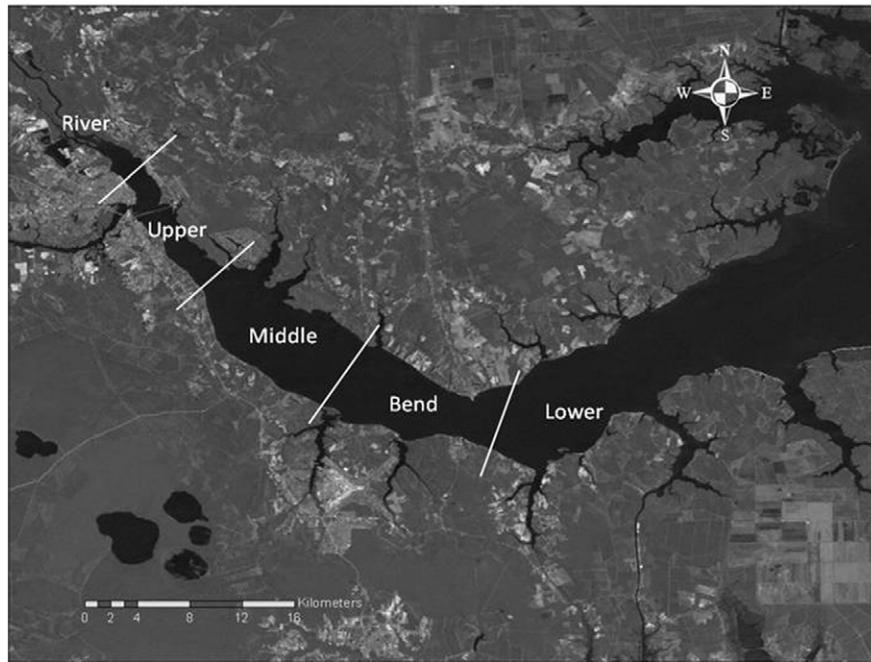


Fig. 2. Neuse River Estuary with designated Use Support Areas as listed in the 303d list and used for TMDL modeling studies.

Estuary segments of the estuary, just upstream from the Bend, tended to have the highest chl *a* values.

The Pamlico River Estuary (PRE) is a continuation of the Tar River system which originates from the fourth largest drainage area in North Carolina (Fig. 3). The freshwater streams and rivers that supply these estuaries originate in the primarily agricultural and wetland/forest areas in the Piedmont area of north central NC and both flow southeasterly until they reach tidal waters and become wide, tidally-dominated estuaries which flow into Pamlico Sound (NCDWQ, 2009, 2010a). In 1989, a Nutrient Sensitive Water strategy was developed

for the Tar–Pamlico River which also had as its goal a 30% reduction in total nitrogen (NCDWQ, 2010a, 2010b). The aim of the strategy was to halt point source increases by allowing “nutrient trading” between point source dischargers and agricultural operations while meeting a 30% nutrient reduction goal. Under the program, dischargers were free to trade reduction debits and credits among themselves, as long as the loading standards for the basin were met (USEPA, 1993). However, even though the targeted point sources have met the 30% reduction goal, total nitrogen concentrations have not shown declining trends and nutrient loads have not fallen below the 1991 baseline load goals.

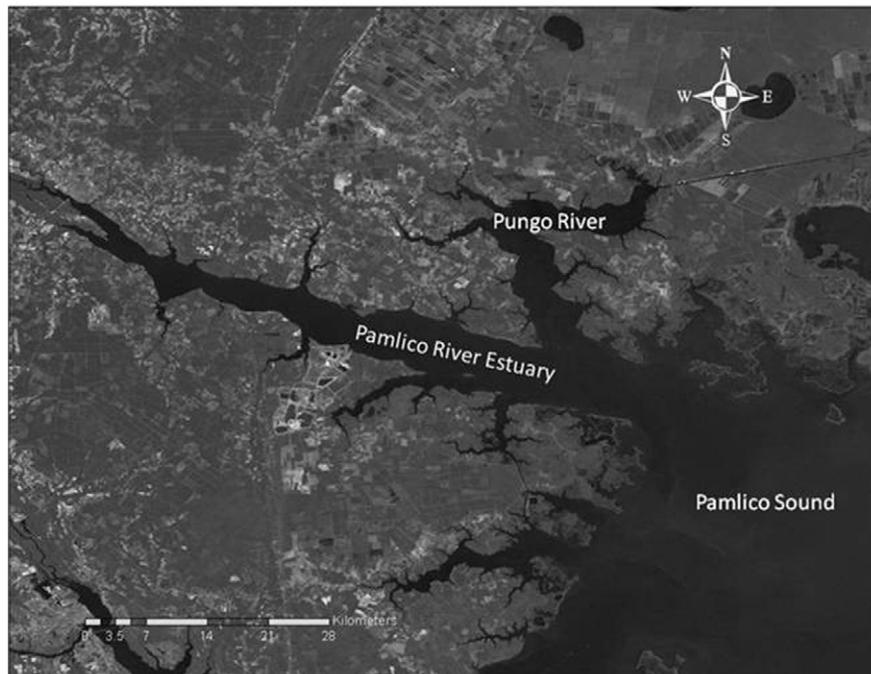


Fig. 3. Pamlico River Estuary including the Pungo River and Pamlico Sound.

This outcome suggested there are other sources of nitrogen (e.g., confined area feeding operations, chemical fertilizers) being input in the system which were not initially accounted for during Phase I modeling (NCDWQ, 2010b). In 1995, the USEPA approved the TMDL with a 30% reduction goal for nutrients in the Pamlico River Estuary based on estuarine response modeling (NCDWQ, 2009).

### 1.2. Satellite remote sensing of chlorophyll *a* in support of nutrient management

The application of remote sensing techniques to water quality assessment in the NRE and Pamlico Sound began in the mid-1980s. The first study to use satellite sensor data to assess the water quality of the Neuse River estuary and Pamlico Sound was published by Khorram and Cheshire (1985). Using Multispectral Scanner (MSS) data from a Landsat-3 overflight conducted in September 1982 and *in situ* data from 75 stations in the Neuse River estuary concurrently sampled by personnel from the North Carolina Division of Environmental Management, the Division of Marine Fisheries, NC Department of Natural Resources and Community Development (NRCD), and the Division of Inland Fisheries, NC Wildlife Resources Commission (WRC), four water quality models were produced that estimated salinity, chlorophyll *a*, turbidity and total suspended solids (TSS) concentrations. This study concluded that additional monitoring was needed in the Neuse River estuary to evaluate the environmental impacts from projected land development in the upper Neuse River watershed (Khorram & Cheshire, 1985).

During 1999, the first aircraft surveys of the Neuse River estuary and Albemarle–Pamlico Sound system were conducted using the NASA Advanced-Infrared Imaging Spectrometer (AVIRIS) flown on the NASA Earth Resources 2 (ER-2) aircraft (Karaska et al., 2004) and the NASA Airborne Oceanographic Light detection and ranging instrument (AOL3) system flown on National Oceanic and Atmospheric Administration research aircraft (Tester et al., 2003). The AVIRIS data, acquired from six flightlines over the Neuse River during 20 June 1999, were used for software evaluation and algorithm development to retrieve chl *a*, suspended matter, colored dissolved organic carbon and water clarity using three Thematic Mapper (TM) equivalent AVIRIS bands. Surface and sub-surface water samples were collected at 25 sites along transects across the Neuse River. The AOL3 acquired measurements of laser-induced fluorescence during four surveys which were converted, using *in situ* measurements from five stations, into chlorophyll *a* and colored dissolved organic matter (CDOM) concentrations.

In 2002, AVIRIS hyperspectral imagery of the Neuse River estuary and Pamlico Sound was again acquired to support algorithm development for water quality indicators. Using these data and field samples collected concurrently from 13 locations along the Neuse River estuary and into Pamlico Sound, Lunetta et al. (2009) determined the optimal spectral bands for water quality monitoring using sensor data, developed, and validated algorithms which estimated chl *a*, colored dissolved organic matter (CDOM), and TSS concentrations. Spectral data from these selected bands were also used to simulate sensor data from the European Space Agency's (ESA) MEdium Resolution Imaging Spectrometer (MERIS). Using three years of satellite imagery (2006–2009) from ESA and approximately 100 *in situ* measurements of chl *a* from the Neuse River Estuary MEdium and MONitoring Project (ModMon; Paerl et al., 2010; Peierls, Hall, & Paerl, 2012) and approximately 1000 chl *a* measurements from the North Carolina Ferry-Based Monitoring (FerryMon; Paerl, 2008; Paerl et al., 2009) program, Sokoletsky, Lunetta, Wetz, and Paerl (2011) developed algorithms which retrieved chl *a*, TSS, and CDOM concentrations from MERIS images of the Neuse River estuary and Pamlico Sound.

Several types of remote sensing platforms and sensors have been used to study the phytoplankton dynamics of the NRE. The objective common to these studies was the development of water quality models

which, with data obtained by satellites or aircraft, could be potentially applied in an operational mode to support nutrient management and compliance. Each of these studies touted the ability of remote sensing platforms and sensors to routinely collect data for these models that would assist government agencies establish and monitor goals for meeting water quality standards (e.g., TMDLs), evaluate the results of water management activities, enforce water quality-related environmental regulations and further understanding of the biological and hydrological characteristics of these aquatic ecosystems and the environmental impacts of the land-use practices within the surrounding environment.

This study is important because for the first time, remotely sensed data were used to directly address issues associated with the management of total nitrogen in the Neuse and Tar–Pamlico River estuaries. During this study, a retrospective assessment of the chlorophyll-based, NC standard for water quality and 10/40 criterion for determining TMDL compliance was conducted using the MERIS case 2 coastal water chlorophyll *a* data product, obtained from the European Space Agency, for the period 2006–2009 to identify times and locations of non-compliance. The study objectives were to: 1) use field-based measurements of chlorophyll and total nitrogen to examine the quantitative relationship that serves as the basis of the 10/40 criterion, 2) assess state water quality and 10/40 compliance using MERIS chlorophyll estimates for the Neuse and Tar–Pamlico River estuaries at daily and annual time scales during the study period, 3) estimate the quantity of estuarine acres impaired by MERIS derived chlorophyll in each estuary during the study period, and 4) evaluate which system wide summary statistic(s) of chlorophyll *a* concentrations (either sample mean, median, and 90th percentile values) at annual time scales would be useful for determining standard and criterion violations and to support environmental compliance monitoring.

## 2. Methods

Total nitrogen (TN) has been designated by the State of North Carolina as the nutrient which, if properly regulated, could limit the excessive growth of phytoplankton in the Neuse River estuary (NCDWQ, 2009). The Neuse River TMDL specifically uses chlorophyll *a* concentration as its endpoint to manage TN concentrations. The general relationship between these variables was examined using linear regression analysis and surface concentrations (collected from 1995 to 2004) from 147 estuaries in Maine, New Hampshire, Massachusetts, Rhode Island, New York, Delaware, New Jersey and North Carolina. These data were collected by the USEPA Mid-Atlantic Integrated Assessment (MAIA-1998), and the National Coastal Assessment (NCA) Programs (2000–2004) as well as the Lower Neuse Basin Association (LNBA-1995 and 1998). Water samples for the MAIA and NCA programs were collected in accordance with EPA National Coastal Assessment field operation procedures (Strobel & Heitmuller, 2001) and chl *a* concentrations were determined fluorometrically (Arar & Collins, 1997). LNBA samples were collected by the University of North Carolina (UNC) Institute of Marine Sciences (IMS) ModMon project and processed in accordance with procedures found in Paerl et al. (2010). For all programs, TN was not measured directly but was calculated as the sum of particulate and total dissolved nitrogen concentrations (B. Peierls – personal communication; MAIA, 2002).

Using ModMon surface chl *a* and TN data from 2006 to 2009 ( $n = 207$ ), the relationship specifically was specifically examined for the Neuse River and Pamlico Sound. Outliers in this dataset were identified from residual analysis of the regressed data and the Interquartile Range Rule (NIST/SEMATECH, 2012). The goodness of fit for the relationship was determined by the  $R^2$  values.

To illustrate the extent and magnitude of eutrophic events in the NRE and PRE, chlorophyll *a* concentrations were derived from 206 atmospherically corrected, MERIS full resolution (FR) ( $300 \times 260$  m pixel size) images subset for the Albemarle–Pamlico area from January 2006

to December 2009. The MERIS images were acquired from the European Space Agency (ESA) by the EPA National Exposure Research Laboratory (NERL) Landscape Characterization Branch (LCB) in 2009. The chlorophyll values in the data files were retrieved from top-of-atmosphere calibrated radiances (Level 1b) that were processed into the MERIS chlorophyll product (Level 2) using the case 2 coastal water algorithm. The algorithm uses the inverse modeling approach to derive three classes of substances which describe the variability of water color. The three classes are defined as 1) phytoplankton pigment with chlorophyll *a* as a proxy, 2) the dry weight of all particles (i.e., the total suspended matter (TSM), and 3) the absorption caused by the dissolved fraction of all water constituents (CDOM or *gelbstoff*) (Doerffer & Schiller, 2007). The MERIS case 2 processor determines the inherent optical properties (IOP) associated with (1) phytoplankton pigment absorption, (2) absorption coefficient of colored dissolved organic matter (CDOM) and bleached particulate matter, and (3) scattering coefficient of total suspended matter (TSM). The IOPs of (1) and (3) are also converted into the concentrations of chlorophyll *a* and TSM dry weight. All three optical components are defined for MERIS band 2 (442 nm). The algorithm is based on a neural network (NN), constructed using simulated data generated from the HYDROLIGHT radiative transfer code (Mobley, 1994) plus a bio-optical model which relates scattering and absorption coefficients to concentrations. The bio-optical model is based on a large data set of measurements of IOPs from cruises in the North Sea, Baltic Sea, Mediterranean Sea and North Atlantic. The NN allows for testing of the measured spectrum is within the scope of the training set. Comparisons with independent test data sets, *in situ* observations and with the MERIS case 1 water algorithm indicated good agreement ([https://earth.esa.int/handbooks/meris/CNTR2-7.htm#\\_Reference\\_documents](https://earth.esa.int/handbooks/meris/CNTR2-7.htm#_Reference_documents); Doerffer & Schiller, 2007; Morel and Antoine, 2011).

### 2.1. Relationship between chlorophyll and total nitrogen in estuarine waters

As previously stated, the Phase II TMDL goal was to achieve compliance of the 10/40 criterion by using chlorophyll *a* as the endpoint to manage total nitrogen concentrations. The relationship between TN and chlorophyll was examined using linear regression analysis and datasets from 1995 to 2004 stored in the EPA Storet system and collected by the USEPA Mid-Atlantic Integrated Assessment (MAIA-1998) and National Coastal Assessment (NCA-2000 through 2004) programs as well as the Lower Neuse Basin Association (LNBA – 1995 and 1998) and ModMon Project (2000–2009). Results are presented for estuaries along the eastern seaboard and specifically for the NRE.

### 2.2. Calibrating MERIS derived chlorophyll values to the waters of the Neuse River Estuary

The Neuse River flows approximately 200 miles from its headwaters in the organic rich, agricultural, and forested landscapes of the piedmont through wetlands of the coastal plain region of eastern North Carolina into Pamlico Sound. Characteristically, waters in the Neuse River basin and estuary contain high concentrations of CDOM, with absorption values ranging from 2 to 6 m<sup>-1</sup> at 440 nm (Vähätalo et al., 2005). In addition, the contribution of phytoplankton to total absorption ranged from 0.1 to 1.4 m<sup>-1</sup> (Vähätalo et al., 2005). For comparison, the range of CDOM absorption used in MERIS processing is 0.005–5.0 m<sup>-1</sup> and for phytoplankton absorption (0.001–2.0 m<sup>-1</sup>) (Doerffer & Schiller, 2007). Given that the ranges of CDOM and phytoplankton absorption used by MERIS during algorithm development overlap with the absorption ranges measured by Vähätalo et al. (2005), it is assumed that absorptive effects of CDOM and phytoplankton on the retrieval of water leaving radiance reflectance spectra have been accounted for during processing by the bio-optical model.

Since the MERIS bio-optical model was developed using IOP measurements from cruises in the North Sea, Baltic Sea, Mediterranean Sea and North Atlantic, the MERIS chlorophyll values in this study were adjusted to chlorophyll concentrations characteristic of estuarine waters of Albemarle–Pamlico Sounds (chl *a*<sub>ambient</sub>). Using *in situ* surface chl *a* concentrations collected by the FerryMon monitoring program (Paerl, 2008) and the NC DWQ Ambient Monitoring System (AMS), a model was derived which tuned the MERIS chlorophyll product to local waters.

FerryMon's water quality monitoring system is installed on three NC Department of Transportation ferries whose routes cross the Neuse River in the Bend segment and along Pamlico Sound (Fig. 4). The heart of the monitoring system is the bbe Algae Online Analyser which operates in flow-through mode to measure chlorophyll fluorescence in real time and quantify algal classes. The system is interfaced with the YSI 6200 data acquisition system which is interfaced with a YSI 6600 multiparameter monitoring sonde. The YSI sensors measure surface water temperature, salinity, dissolved oxygen, pH, chlorophyll *a* (by fluorescence), and turbidity. Global Positioning System (GPS) time-stamped sensor data are stored in the data acquisition system and are sent nightly from the ferry by wireless internet connection to the UNC IMS laboratory (B. Peierls – personal communication).

The AMS consists of a network of stations established to provide site-specific, long-term water quality information on significant rivers, streams, and estuaries throughout the state of North Carolina. There are approximately 29 Lower Neuse River Basin monitoring stations. Some stations are sampled monthly, others are sampled on a weekly basis. Physical data such as dissolved oxygen, pH, temperature, and salinity are recorded at each station. Water samples are also collected at each station for turbidity, TSM, nutrients, chlorophyll and fecal coliform. Chlorophyll *a* concentrations were determined in accordance with EPA Method 445 (modified option; Arar & Collins, 1997).

In this study, chlorophyll data were used from 19 ferry crossings during 2006–2009 of the Neuse River estuary between Cherry Branch and Minnesott Beach, NC along the Neuse River Bend and Lower Neuse River Estuary segments (Fig. 4; Cherry Branch/Minnesott transect) and in Pamlico Sound (Fig. 4; Cedar Island/Orcacoke and Swan Quarter/Orcacoke transects). Data were also used from 11 AMS stations sampled from 2008 to 2009 also along the Lower Neuse River Estuary segment. The *in situ* data used in the analysis were selected to coincide with dates and times of MERIS overflights.

Using Type I linear regression, a semi-empirical model was developed to predict chl *a* concentrations calibrated for the Neuse and Tar–Pamlico River estuaries from MERIS chlorophyll values. The accuracy of the correction algorithm was assessed by calculating the Root Mean Square Error (RMSE) of the corrected chl *a* concentrations from:

$$\text{RMSE} \left( \frac{\mu\text{g}}{\text{L}} \right) = \sqrt{\frac{\left( \sum \text{Chl } a \text{ measured} - \text{Chl } a \text{ predicted} \right)^2}{N-1}} \quad (1)$$

### 2.3. Assessing 10/40 criterion compliance and chlorophyll exceedances Based on MERIS derived chlorophyll

The 10/40 criterion does not define or specify a time period (daily, weekly, monthly, or annually) for determining TMDL compliance. In this study, daily compliance of the criterion for the Neuse and Tar–Pamlico estuaries was evaluated in an EXCEL spreadsheet using chl *a*<sub>ambient</sub> data derived from each MERIS image. During this analysis, the number of pixels (i.e. EXCEL spreadsheet cells) with chl *a*<sub>ambient</sub> concentrations greater than 40 μg/L were summed for each image and converted into a percentage of the total number of pixels in that image for each estuary. That percentage was then interpreted to determine if violations of the 10/40 criterion had occurred based on the following question: Did fewer than 10% of the pixels observed from a

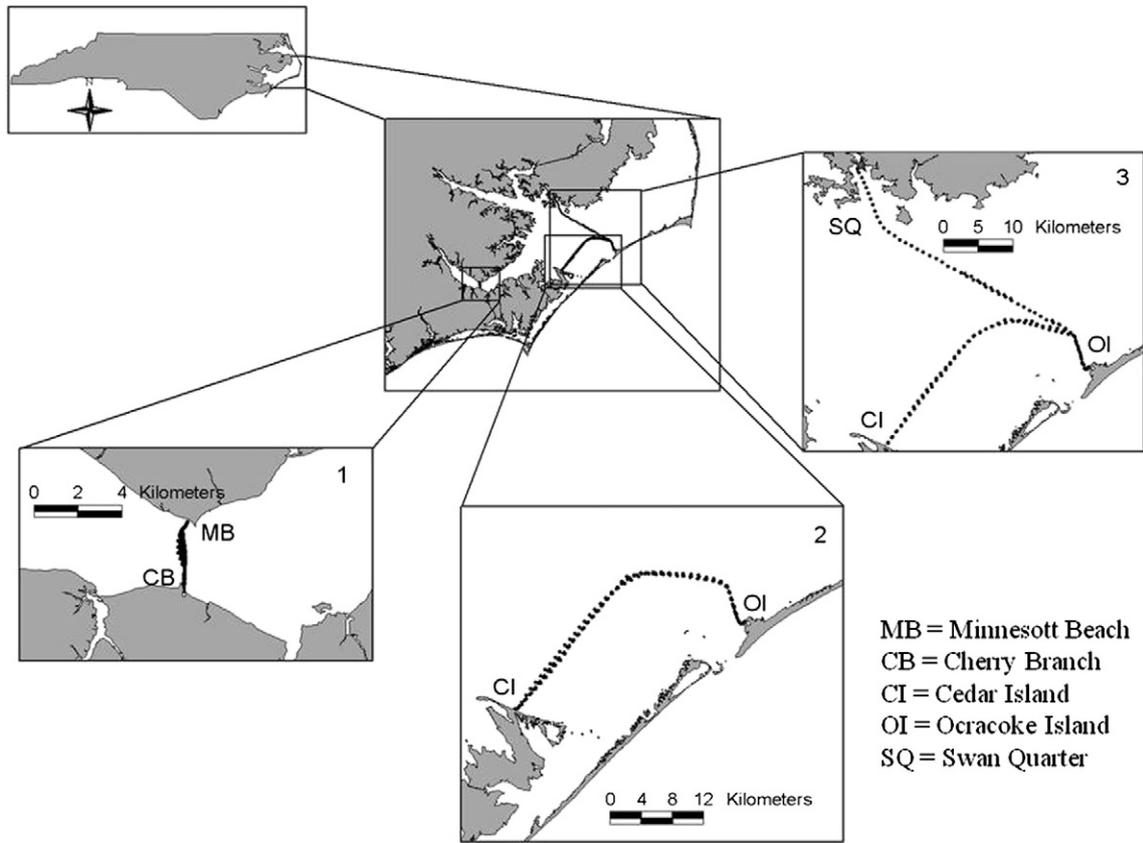


Fig. 4. Maps depicting ferry route 1 in the Neuse River Estuary and ferry routes 2 and 3 that traverse Pamlico Sound (modified from Paerl, 2008).

daily MERIS image for the NRE or PRE estuary exceed  $40 \mu\text{g/L}$ ? For images that exceeded the 10% threshold, the distribution of chl  $a_{\text{ambient}}$  concentrations was mapped using ArcMap10 to visually illustrate the spatial dimensions and locations of 10/40 criterion and water quality standard violations in the NRE and PRE. Compliance with the 10/40 criterion for the Neuse and Tar–Pamlico estuaries was also evaluated on an annual basis by aggregating the number of pixels that violated the 10/40 criterion for a given year and dividing by the total number of chl  $a_{\text{ambient}}$  pixels for all MERIS images during that period. The resulting percentage of pixels  $>40 \mu\text{g/L}$  was used to determine TMDL status based on the following question: Did fewer than 10% of the samples collected in an estuary in a year exceed  $40 \mu\text{g/L}$ ?

The estuarine area that exceeded the chl  $a$  standard was determined by summing the number of pixels with chl  $a_{\text{ambient}}$  estimates in excess of  $40 \mu\text{g/L}$  for each MERIS image and converting pixel dimensions to acres (1 pixel  $\approx 19$  acres). The impacted acres values were plotted versus time to assess the spatial distribution of impairment for each estuary from 2006 to 2009.

The arithmetic mean, median, and 90th percentile concentrations of chlorophyll were calculated for each MERIS image to evaluate which measure would provide the most accurate indicator of 10/40 criterion exceedance and most protective of designated uses. The arithmetic mean (sample mean) for the chlorophyll  $a$  values in an image was expressed as the sum of all chl  $a_{\text{ambient}}$  values divided by the number of pixels. The median for the chlorophyll  $a$  values (i.e., 50th percentile) for each image was defined as the numerical value that separated the higher half of the chl  $a$  dataset from the lower half. The 90th percentile value was determined to assess the magnitude of phytoplankton blooms by identifying the largest 10% of the chl  $a_{\text{ambient}}$  estimates in an image. The summary statistics were presented as scatterplots of each parameter versus time and compared with the  $40 \mu\text{g/L}$  standard to indicate periods of exceedance.

### 3. Results

#### 3.1. Relationship between chlorophyll and total nitrogen in estuarine waters

Results indicated that there is a robust linear relationship between TN and chl  $a$  in data used in this study (Fig. 5). For east coast estuaries ( $n = 142$ ), there is a strong statistical relationship ( $R^2 = 0.70$ ) with a standard error of  $4.6 \mu\text{g/L}$  chl  $a$ . In Pamlico Sound ( $n = 225$ ), the results also showed a strong statistical relationship ( $R^2 = 0.73$ ) and with a standard error of  $2.3 \mu\text{g/L}$ . In the Neuse River estuary ( $n = 270$ ), the results again showed a robust relationship ( $R^2 = 0.76$ ) with a standard error of  $5.4 \mu\text{g/L}$ . From these relationships, a chlorophyll-based TMDL for total nitrogen can be estimated using the NC chl  $a$  standard as a guide. At a chl  $a$  value of  $40 \mu\text{g/L}$ , a TMDL for TN in the Neuse River estuary could range between 900 and 1100  $\mu\text{g/L}$  (Fig. 5). For comparison, the chlorophyll  $a$  standard for restoration programs in Chesapeake Bay is  $15 \mu\text{g/L}$ . If applied as a standard for the Neuse River, a TMDL for TN could range from 400 to 800  $\mu\text{g/L}$ . Concentrations greater than  $15 \mu\text{g/L}$  are considered large enough to shade and hinder the growth of sea grass and other submerged aquatic vegetation (SAV) (Batiuk et al., 2000).

#### 3.2. Calibrating MERIS derived chlorophyll values to the waters of the Neuse River Estuary

Using regression analysis, an algorithm was derived which calibrated MERIS chl  $a$  values to estimates comparable to *in situ* values ( $n = 30$ ) measured by FerryMon and NCDENR Ambient Monitoring Station (AMS) instruments (Eq. 2):

$$\text{Chl } a_{\text{calibrated}} = 1.3671 \times (\text{MERIS chl } a \text{ values}) - 11.283 \quad (2)$$

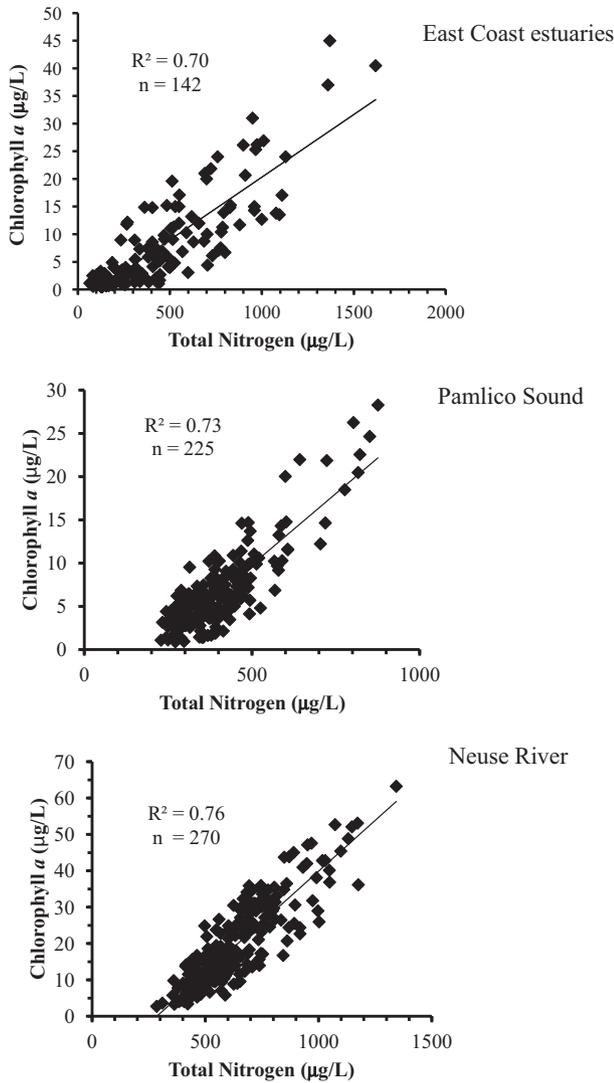


Fig. 5. Relationship between total nitrogen and chlorophyll *a* for East Coast estuaries, Pamlico Sound, and Neuse River estuary. Data collected by US EPA MAIA, USEPA NCA, NCDENR, NOAA, LNBA, and UNC IMS.

The algorithm was developed from chl *a* retrieved from the MERIS data product and *in situ* chl *a* estimated from fluorescence measurements at NCDENR AMS water quality stations ( $n = 11$ ) during winter and summer 2008 as well as Spring 2009 (Fig. 6). *In situ* chl *a* was also used from fluorescence measurements collected as part of the FerryMon program during routine ferry crossings ( $n = 19$ ) of the lower NRE and Pamlico Sound during winter 2006, summer 2007, spring 2008, spring and summer 2009. There were 30 MERIS images that were coincident with dates that the ambient chlorophyll data. The scatterplot showed a strong statistical relationship ( $R^2 = 0.84$ ) between *in situ* chl *a* and chl *a* retrieved from the MERIS data.

The algorithm was validated using ModMon *in situ* chl *a* and chl *a* retrieved from the MERIS images ( $n = 120$ ) collected within 1 day of the sensor overpass (Fig. 7). There were 14 MERIS images and ModMon sampling dates that met these criteria. The datasets represent surface water chlorophyll concentrations from winter 2007 through fall 2009. The ModMon data consisted of chlorophyll values that were collected on a bi-weekly basis at water quality sampling stations in the mid channel section of the estuary from the upper NRE into Pamlico Sound. Regression of the *in situ* chl *a* data against MERIS chl *a* data calibrated using Eq. (2) showed a strong linear, statistical relationship ( $R^2 = 0.87$ ) between measured and predicted values (Fig. 7) with an RMSE

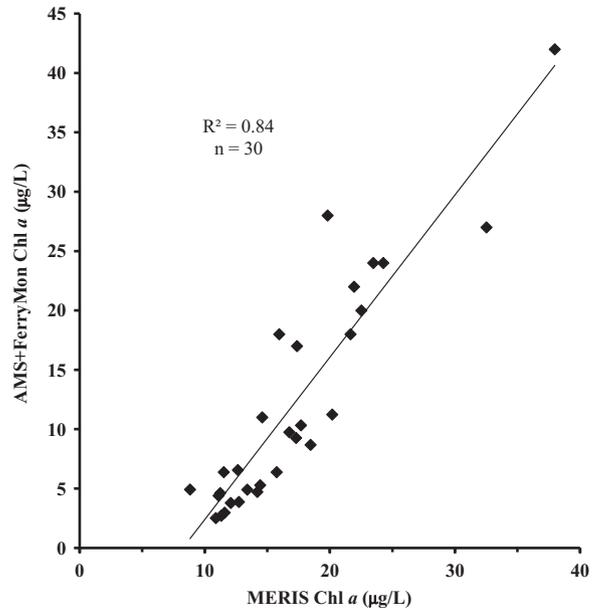


Fig. 6. Relationship between chl *a* measured by FerryMon and NCDENR AMS instruments and MERIS chl *a*.

of 7.6 µg/L (Fig. 5). The  $R^2$  values are somewhat better than those of Sokoletsky et al. (2011) ( $R^2 = 0.70$ ) who compared chl *a* concentrations estimated from atmospherically corrected MERIS spectral data with NRE FerryMon chl *a* data only.

### 3.3. Assessing 10/40 criterion compliance and chlorophyll exceedances based on MERIS derived chlorophyll

During 2006–2009, the MERIS data from both estuaries contained a minimum of 140 to greater than 2300 samples (1 pixel = 1 sample) at chl  $a_{\text{ambient}}$  concentrations 40 µg/L or greater. Of the four year dataset, the period from January to May 2007 in both the Neuse and Pamlico River estuaries exhibited the largest phytoplankton blooms and the greatest percentage of samples with chl  $a_{\text{ambient}}$  concentrations more than 40 µg/L (Figs. 8 and 9). MERIS chl  $a_{\text{ambient}}$  concentrations of 40 µg/L or greater occurred in at least 20% of image pixels and declined to a low of 4% for the entire NRE during this period. These percentages indicated a large-scale spatial and temporal exceedance of the NC

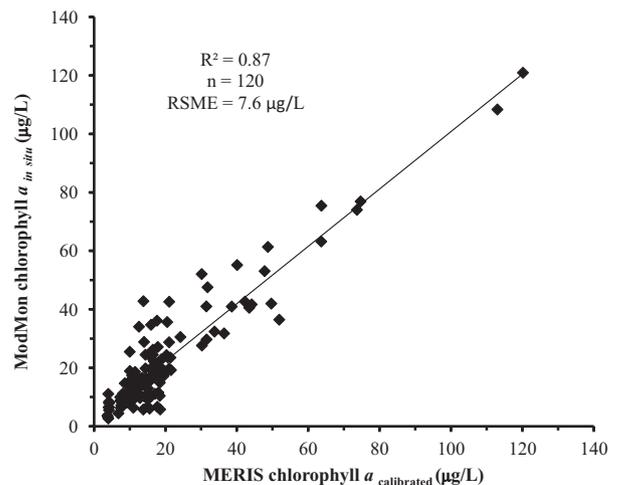


Fig. 7. Relationship between MERIS chl  $a_{\text{calibrated}}$  derived from Eq. (2) and Chl *a* measured from ModMon stations.

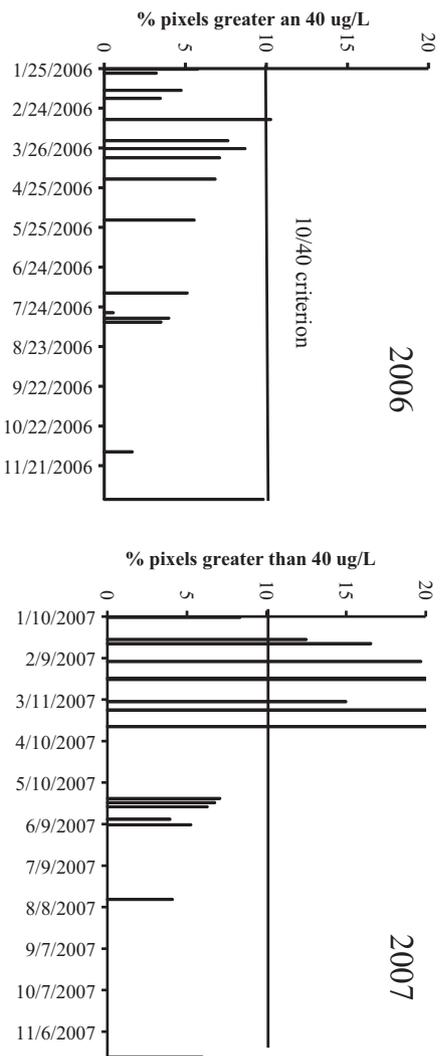


Fig. 8. Neuse River Estuary percentage of pixels greater than 40  $\mu\text{g/L}$  and time periods of 10/40 criterion exceedance from 2006 to 2009 based on MERIS data.

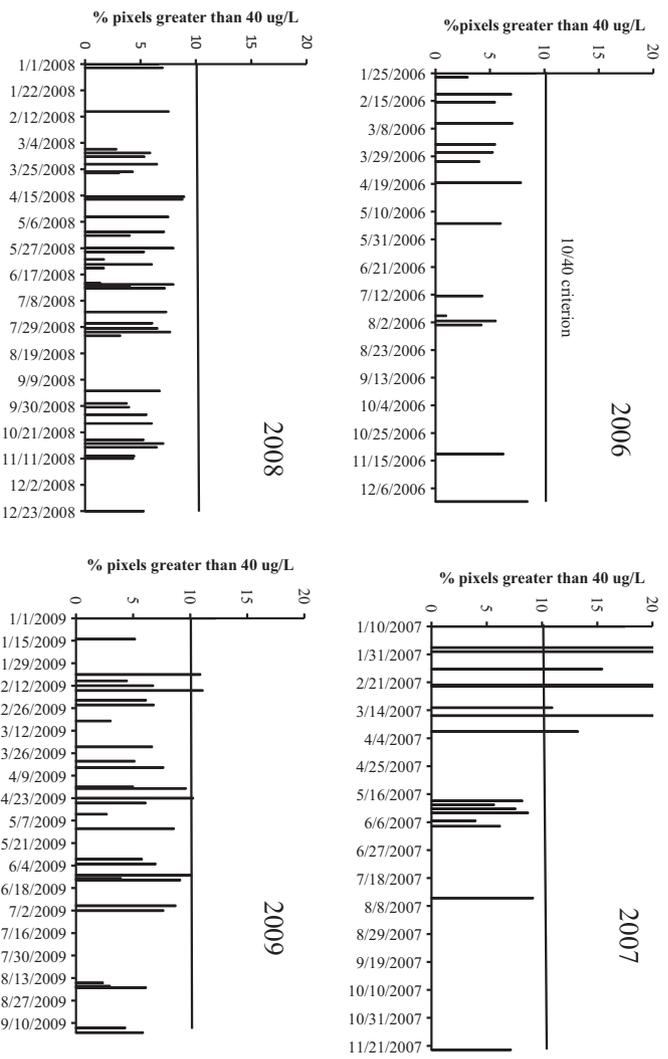


Fig. 9. Pamlico River Estuary percentage of pixels greater than 40  $\mu\text{g/L}$  and time periods of 10/40 criterion exceedance from 2006 to 2009 based on MERIS data.

water quality standard and the 10/40 criterion of the TMDL that persisted over several months.

3.4. Neuse River Estuary: winter–spring 2007

The magnitude and spatial distribution of MERIS chl *a*<sub>ambient</sub> concentrations of the NRE and PRE were mapped using ArcMap 10 to illustrate the locations of exceedances of the state water quality standard and the 10/40 criterion (Figs. 10 and 13). Beginning in late January 2007, the Bend and Lower segments of the NRE were the sections characterized with the largest phytoplankton blooms (Fig. 10). Between January–May 2007, the largest blooms moved seaward and were primarily confined to the Lower Use area. However, lower intensity blooms were observed in the Bend. Field measurements in the Bend at ModMon Station 120 (Fig. 11) during this period indicated that peak chlorophyll concentrations ranged between 80 and 180 µg/L between January and April 2007 (Paerl et al., 2010). The MERIS images suggested that these high concentrations may have emerged from rivers and streams along the north and south shores of the estuary and coalesced in the estuary channel or are the product of localized upwelling events and cross-estuary oscillations (“sloshing”; Luettich et al., 2000; Paerl et al., 2009) that are known to occur between the northern and southern shores of the Neuse Estuary.

The location of the chlorophyll maximum observed in the MERIS images, during winter–spring 2007, occurred in the Bend and Lower

Use sections of the Neuse River estuary generally in the vicinity of ModMon Stations 120 and 140 (Fig. 11). This position contrasted with the commonly held view, based on year round observations, that the Upper and Middle Use sections of the estuary tended to have the highest chlorophyll *a* concentrations. This change may be explained by the dramatic influence that climatic events (e.g. Nor’easters, tropical storms, and hurricanes) have on changing the hydrologic nature and nutrient dynamics of the Neuse and Pamlico River estuarine systems (e.g., Paerl et al., 2010). Paerl et al. (2010) and Paerl (2009) have shown that the loading of dissolved inorganic nitrogen (DIN) at the head of the NRE increased in response to increased rainfall associated with Hurricanes Fran (1996), Dennis and Floyd (1999) and tropical storm Ernesto (2006). Further, they have shown that low freshwater discharge during periods of extreme droughts resulted in low nutrient loading to the NRE.

The MERIS time series, when combined with hydrologic data for the study period, suggested that increased freshwater discharge and nutrient loadings caused by tropical storm Ernesto and a late fall 2006 Nor’easter were responsible for pushing the chlorophyll maximum downstream to the lower sections of the NRE. During September 2006, tropical storm Ernesto brought more than 5 in. of rain to eastern North Carolina which caused freshwater flooding in low-lying areas, as well as along major and minor roadways (Roth, 2007). During late fall 2006, specifically between November 21 and 23, an extratropical cyclone (known as the 2006 Nor’easter) brought more than 7 in. of

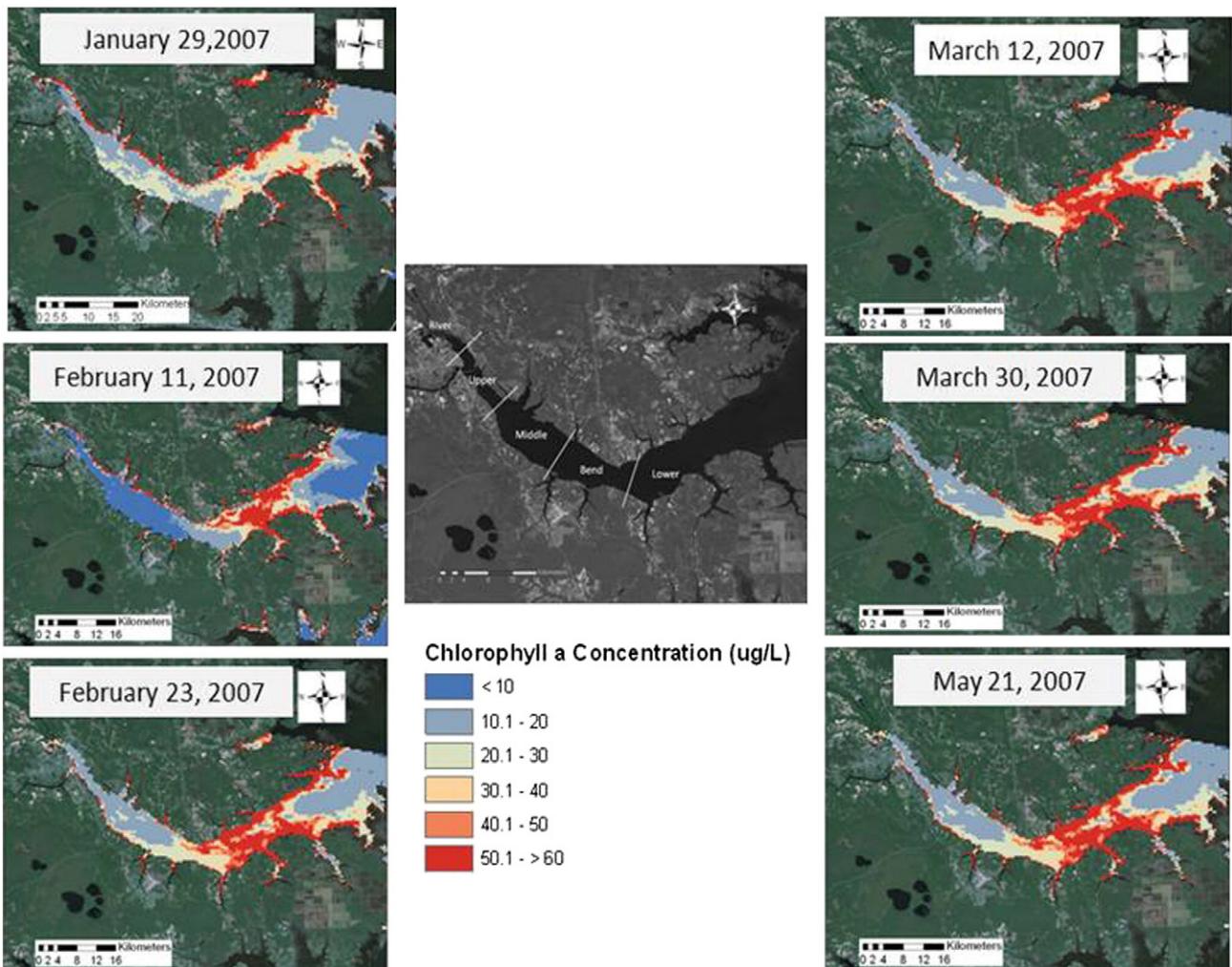


Fig. 10. Daily time series of NC water quality violations and 10/40 criterion non-compliance in the Neuse River Estuary from January to May 2007 in response to the 2006 Nor’easter during late Fall 2006. Intended for color reproduction on the Web and in print.

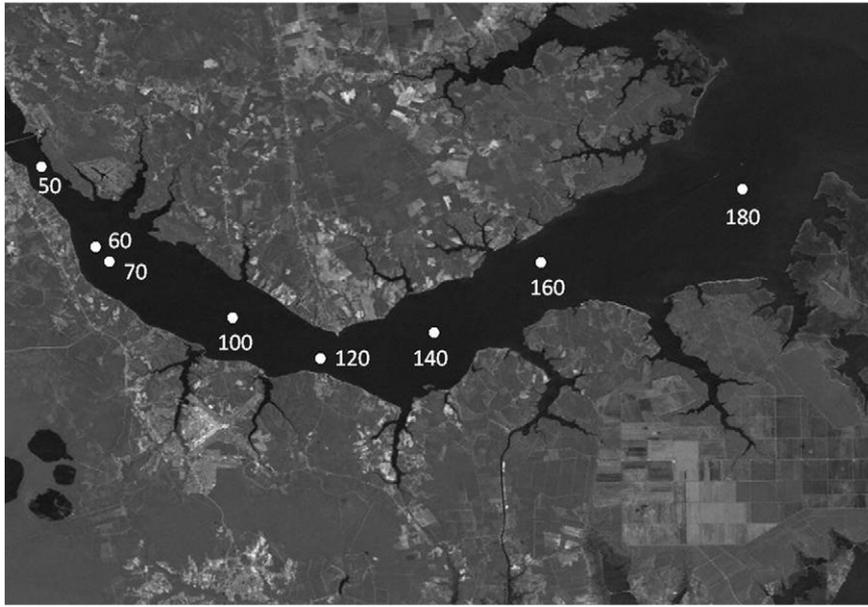


Fig. 11. Location of ModMon water quality sampling stations in the Neuse River.

rain ([www.erh.noaa.gov/rah/events](http://www.erh.noaa.gov/rah/events)) to southeastern North Carolina. During this period, daily streamflow data, measured at USGS gauge Station 02089500 (Kinston, NC), located approximately 60 km from the head of the estuary, showed streamflow increased from approximately  $30 \text{ m}^3 \text{ s}^{-1}$  in late Summer 2006 to a peak of approximately  $200 \text{ m}^3 \text{ s}^{-1}$  in November 2006 and slowly subsided through June 2007 returning to approximately  $30 \text{ m}^3 \text{ s}^{-1}$  (Fig. 12a). The downstream effect of increased freshwater discharge associated with these events, as recorded in Bend area at ModMon Station 140 (Fig. 11) located more than 200 km from the USGS gauging station, was a 10 ppt salinity decrease and 20 degree drop in water temperature by December 2006. Reduced salinities and temperatures continued at this location until June 2007 (Fig. 12b and c). The nutrient regime at ModMon Station 140 also changed in response to the increased streamflow as the loading of total nitrogen to the lower estuary increased by a factor of five from  $500 \mu\text{g/L}$  during mid-November 2006 to a peak of more than  $2000 \mu\text{g/L}$  during late February 2007 and approximately  $1500 \mu\text{g/L}$  in late March 2007 (Fig. 13a). Concurrently, chlorophyll concentrations at ModMon Station 140 continued to rise from approximately  $20 \mu\text{g/L}$  in late December 2006 to very high concentrations (approximately  $80 \mu\text{g/L}$ ) in late February 2007 and peak concentrations (approximately  $140 \mu\text{g/L}$ ) in late March 2007 (Fig. 13b).

In comparison, from May to November 2007, the NRE showed a dramatic reduction in water quality exceedances. The decline in exceedances and the increased water quality could be attributed to the onset of abnormally dry to severe drought conditions upstream in the Neuse River watershed during much of summer and fall 2007 (NC Drought Management Advisory Council, 2007; Weiz et al., 2011). During this period, pixels with chl *a* concentrations  $>40 \mu\text{g/L}$  varied from 9.1% in May to 5.9% in June (Fig. 8). Streamflow also decreased to less than  $30 \text{ m}^3 \text{ s}^{-1}$  (Fig. 12a) and the instantaneous loading of DIN decreased to less than  $10 \text{ g s}^{-1}$  (Paerl et al., 2010).

### 3.5. Pamlico River Estuary: winter–spring 2007

A satellite-derived time series of water quality standard exceedances over the same 5 month period as the NRE was prepared for the PRE (Fig. 14). During this period, the PRE and adjoining creeks and rivers were also impacted by increased rainfall and nutrient loadings associated with tropical storm Ernesto and the 2006 Nor'easter. MERIS images

contained an average of 627 pixels with chl *a*<sub>ambient</sub> values of  $40 \mu\text{g/L}$  or greater. Similar to NRE, the 29 January image of the PRE is characterized by very large phytoplankton blooms ( $50 \mu\text{g/L}$  and greater) in the freshwaters of the Tar River (on the upper left side of the image), along the length of the Pamlico River (chl *a*  $30 \rightarrow 50 \mu\text{g/L}$ ) to the entrance to Pamlico Sound. Spatially, approximately 28% of the pixels in the image contained chl *a*<sub>ambient</sub> values greater than  $40 \mu\text{g/L}$ . Concentrations  $>50 \mu\text{g/L}$  were observed emerging from creeks along the south and north shores of the estuary. Over the same period, the PRE was out of compliance as 13% to 28% of the chl *a*<sub>ambient</sub> values exceeded both the water quality standard and the 10/40 criterion on a daily basis (Fig. 9). In contrast with the NRE where high chlorophyll concentrations persisted through spring and into summer, chlorophyll levels in PRE declined to  $10\text{--}20 \mu\text{g/L}$  by late May (Fig. 14). Comparatively, the Pungo River estuary, located in the PRE system, remained in compliance with the state standard and the 10/40 criterion during much of winter/spring 2007.

Pamlico River MERIS datasets from 2008 exhibited the lowest number of exceedances for both the water quality standard and the 10/40 criterion during the 4 year study period. For all 42 datasets from that period, the range of water quality exceedances varied from a high of 8.9% in April to a low of 1.7% in June (Fig. 9). The dramatic decrease could be attributed to below average flow condition in the Tar River brought about during the peak of exceptional drought conditions in 2007–2008 (Wetz et al., 2011).

In 2009, the Pamlico River from the winter to late spring and during summer seasons showed that 12.2%, 10.9%, 11.1%, 10.2 and 10.1% of the calibrated chlorophyll values both exceeded the water quality standard and the 10/40 criterion (Fig. 9). The increase in the number of exceedances in both the water quality standard and the 10/40 criterion may be the result of a return to normal flow conditions in the estuary during winter 2008–spring 2009 (Wetz et al., 2011). However, the increased freshwater flow led to stratification which resulted in hypoxic conditions and generated significant fish kills (Wetz et al., 2011).

The MERIS data used in this study strongly support the conclusions of previous research publications (e.g., Paerl, 2009; Paerl et al., 2010) that hydrologic variability which occurs in response to large climatic events plays an important role in the mobilization, processing and delivery of nutrients to sounds and bays in the Neuse and Pamlico estuarine systems.

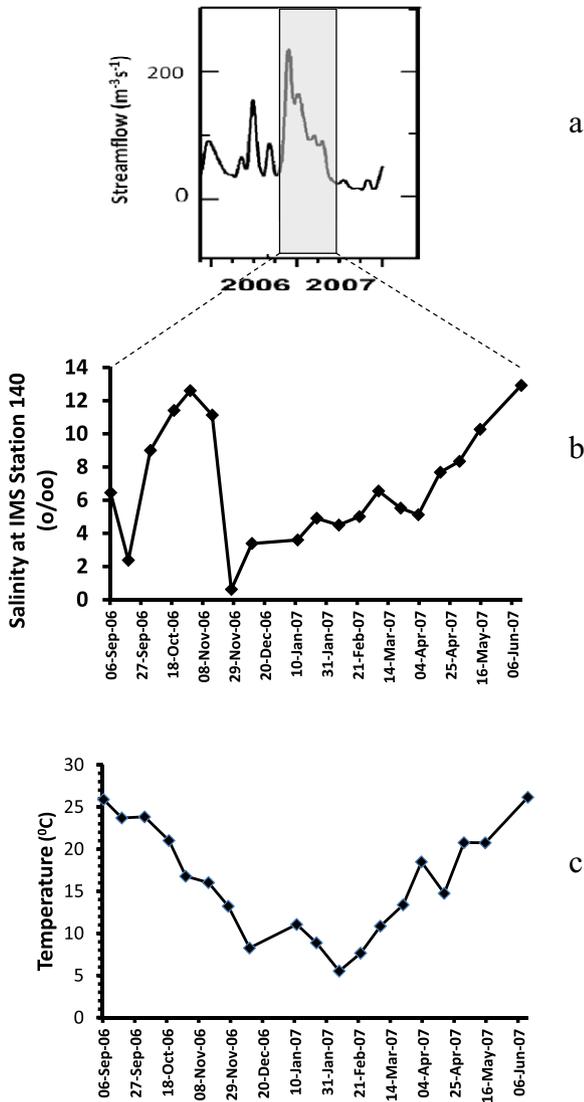


Fig. 12. a.) Neuse River daily mean streamflow measured at USGS gauge station 02089500 at Kinston NC from January 2008 to December 2007 (modified from Paerl et al., 2008). The shaded area represents September 2006–June 2007, b) Salinity time series from ModMon station 140 in the Lower Neuse River from September 2006 to June 2007, and c) surface temperature at station 140 from September 2006 to June 2007.

3.6. Annual spatial extent of phytoplankton distributions along the Neuse and Tar–Pamlico River estuaries and adjoining Pamlico Sound

The daily satellite-derived chlorophyll concentrations were composited on an annual basis to identify those areas within the NRE (Fig. 15) and PRE (Fig. 16) that consistently exceeded the state water quality standard and the 10/40 criterion for any year of interest.

During this process, the number of MERIS chl *a* datasets used for the Neuse River estuary varied from a minimum of 12 in 2006 to a maximum of 34 in 2008. Interestingly, the data showed that exceedances occurred in all Use Support Areas over the four year period. From 2006 to 2009, exceedances and near exceedances were observed in the River segment mainly along the northern shoreline (Fig. 15). Pixels in this area routinely contained values in excess of the water quality standard suggesting localized nutrient input either from upwelling periods, marinas, waste water treatment plants, and/or discharging groundwater sources (Spruill & Bratton, 2008; Tesoriero, Duff, Saad, Spahr, & Wolock, 2013).

In 2006, exceedances of the water quality standard and 10/40 criterion non-compliance, also occurred in the River and Upper segments

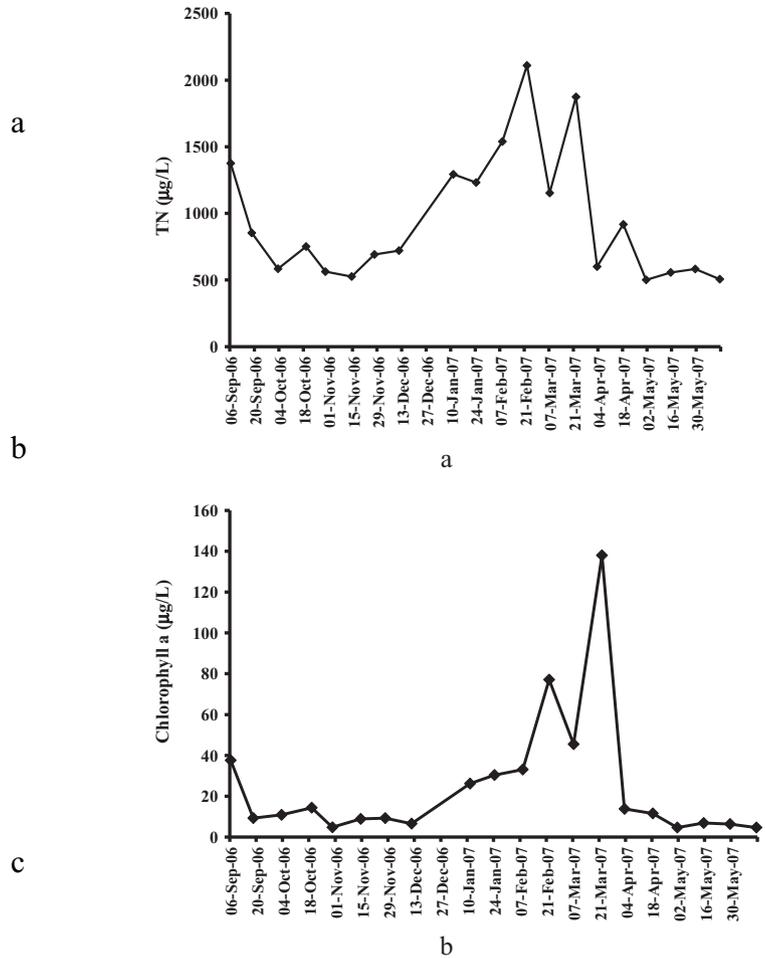
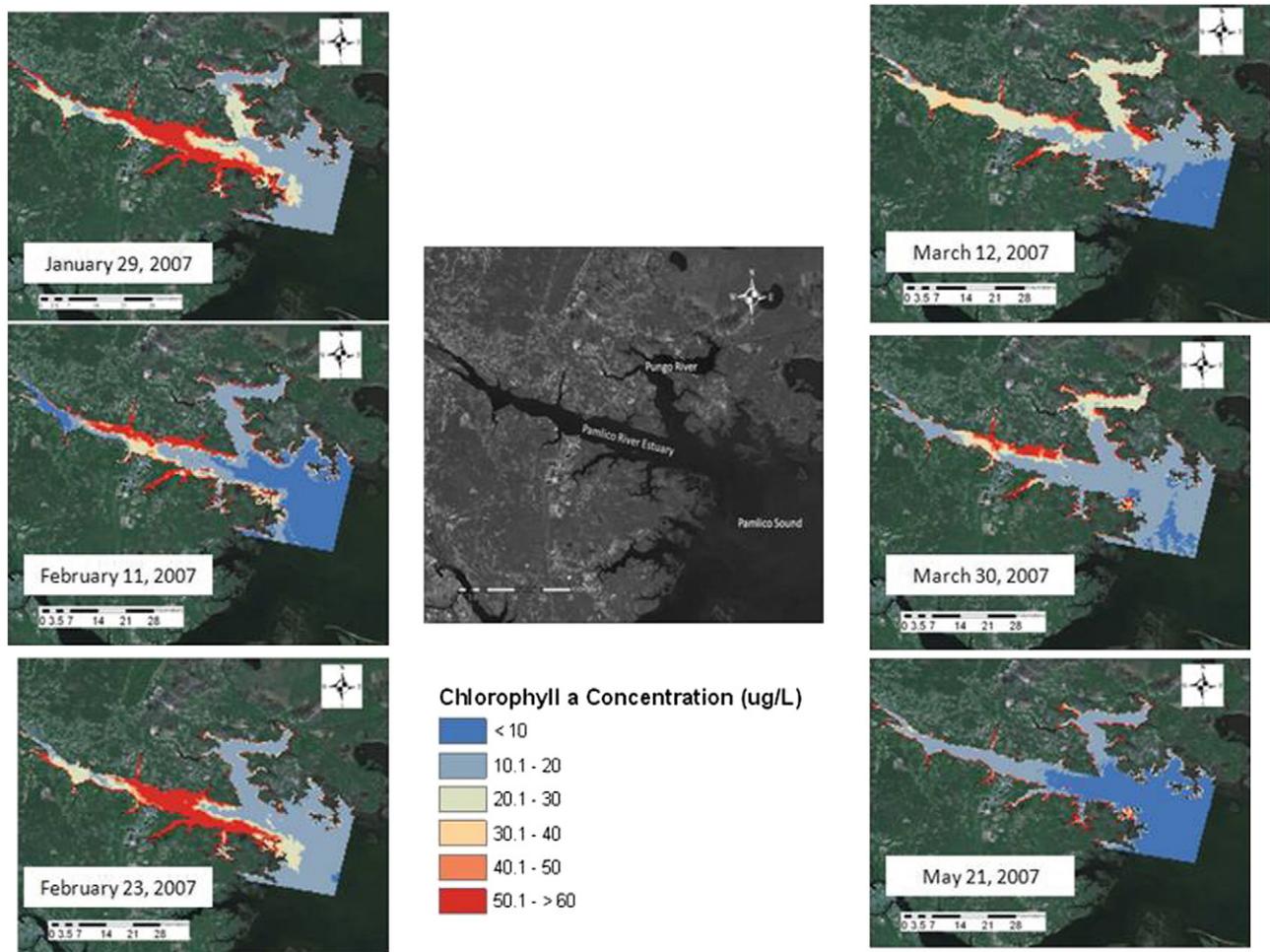


Fig. 13. a) Total nitrogen concentrations from September 2006 to June 2007 at ModMon Station 140 in the Lower Neuse River. b) Chlorophyll concentrations at ModMon Station 140 over the same time period.

(Fig. 15). Field monitoring data indicated that from 2002 to 2006, the standard was exceeded 12 and 23% of the time at two stations in the Upper segment (NCDWQ, 2009). These segments have been classified by NCDENR as impaired for aquatic life due to high chlorophyll concentrations with a maximum concentration of 239 µg/L along the center of the estuary in the Upper segment (NCDENR, 2009). In 2007, the footprint of the 2006 Nor'easter event is seen as the areas of highest chlorophyll concentrations have moved seaward from the upper estuary to Lower segment. This segment was classified as Impaired for aquatic life due to high chlorophyll *a*. Field data indicated that exceedances occurred 11 and 18% of the time at two stations in this segment from 2002 to 2006 (NCDWQ, 2009). The highest chlorophyll *a* concentration encountered in the field was 158 µg/L along the north shore of the estuary. There were no water quality standard or non-compliance violations along the main channel of the estuary in the other use segments. However, exceedances of the state standard and non-compliance of the 10/40 criteria occurred as pixels with concentrations greater than 40 µg/L observed along the north shore and in creeks and rivers of the south.

During the drought year of 2008, the composited data indicated that the entire main channel of the estuary was generally in compliance. However, pixels with concentrations greater than 40 µg/L were again observed along the north shore of the Upper, Middle, and Bend segments and in feeder creeks and rivers along the south shore. During 2009, exceedances and non-compliance were again confined to the north shore of the River, Upper, Middle and Bend segments with persistent excess chlorophyll in creeks and rivers of the south shore. It should



**Fig. 14.** Daily time series of NC Water Quality Standard Violations and 10/40 criterion non-compliance in the Pamlico River Estuary from January to May 2007 in response to Tropical Storm Ernesto during late Fall 2006 and rainy Winter 2007. Intended for color reproduction on the Web and in print.

be noted that high concentrations of chlorophyll ( $>30 \mu\text{g/L}$ ) persisted in the main stem of the Middle-Bend segments during the period.

For the Pamlico River estuary, the number of datasets varied from a minimum of 16 in 2006 and 2007 to a maximum of 33 in 2008 (Fig. 16). Because the PRE was not segmented according to Use categories like the Neuse River estuary, the estuary has been divided in this study into Tar River, Upper, Middle and Lower sections to describe the predictions of water quality. In 2006, the composited MERIS images indicated that the entire estuary was generally in compliance from a water quality standard and 10/40 criterion perspective. However, increased chl *a* concentrations, probably due to localized nutrient inputs, were observed along the south shore of the Upper segment but concentrations were not large enough to be classified as violations. NCDWQ monitoring ( $n = 24$ ) indicated that, for this segment, maximum chlorophyll concentrations reached  $38 \mu\text{g/L}$ ; mean value of  $10 \mu\text{g/L}$ ; and median value of approximately  $5 \mu\text{g/L}$  (NCDWQ, 2010a).

In 2007, the footprint of the 2006 Nor'easter event is seen as the middle to lower sections of the estuary were out of compliance as large plumes with high chlorophyll concentrations emerge from the northern and southern shores (Fig. 16). NCDWQ monitoring ( $n = 24$ ) in middle section indicated that annual chlorophyll *a* concentrations reached a maximum of  $76 \mu\text{g/L}$ ; mean value of approximately  $25 \mu\text{g/L}$ ; and median value of approximately  $15 \mu\text{g/L}$  during the period (NCDWQ, 2010a).

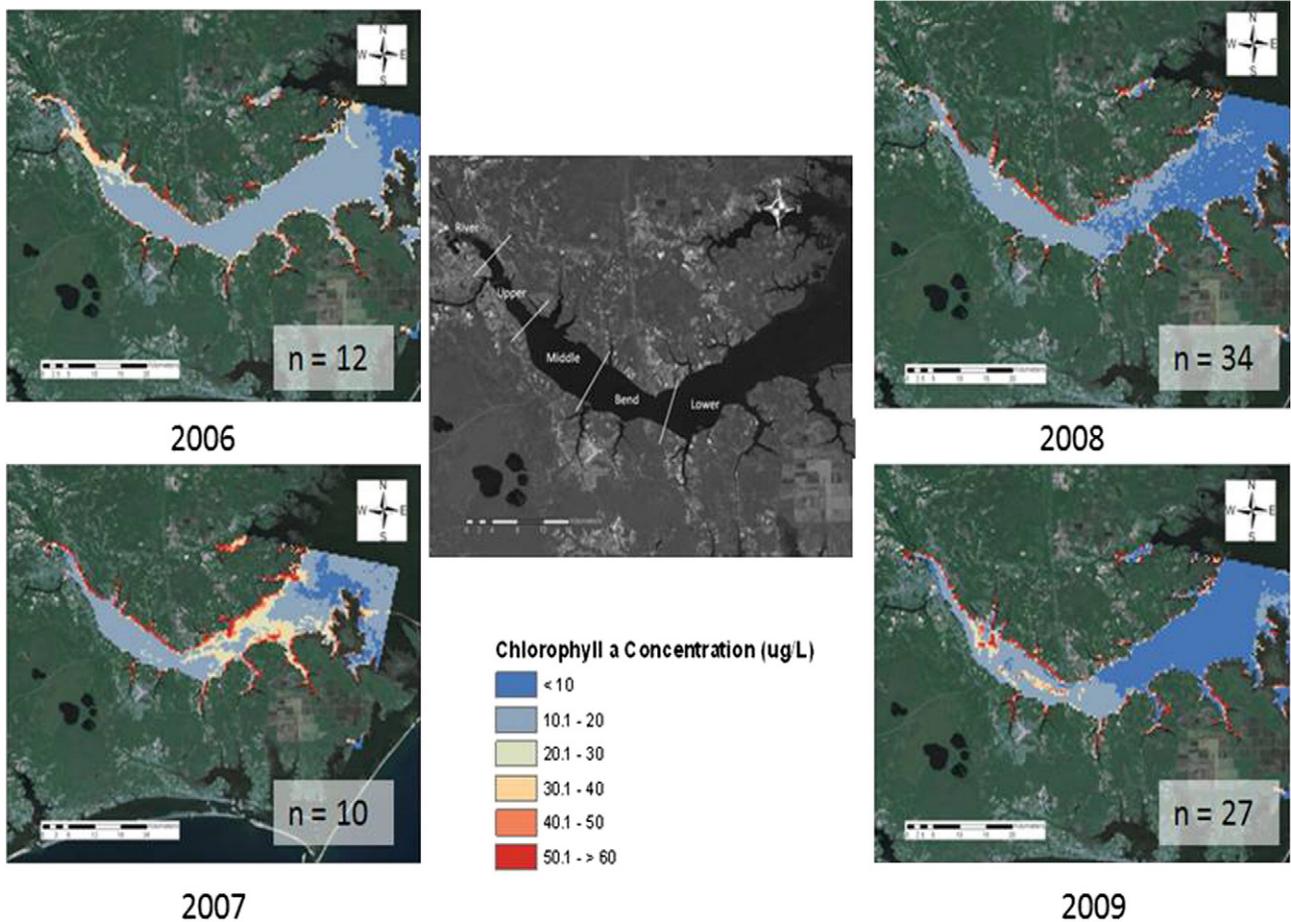
MERIS chlorophyll results from 2008 and 2009 indicated that exceedances and non-compliance are generally confined to the upper Pamlico River estuary. NCDWQ monitoring in 2008 ( $n = 24$ ) indicated

that annual chlorophyll *a* concentrations reached a maximum  $66 \mu\text{g/L}$  with mean and median values of approximately  $35 \mu\text{g/L}$  during the period (NCDWQ, 2010a).

### 3.7. Assessment of the quantity of estuarine area impaired due to excess chlorophyll concentrations

The first complete evaluation of the full spatial extent of impairment due to chlorophyll in the Neuse River Estuary, from headwaters to Pamlico Sound, by the NCDWQ did not occur until the 2009 Neuse River Basin Report and covered the assessment period of January 2002 to December 2006. Prior to this report, NCDWQ had been unable to assess improvement in response to nutrient reduction due to the lack of sufficient data for comparison (NCDWQ, 2009).

In this study, additional information is provided for evaluating the area impaired due to chlorophyll *a* standard violations in the Neuse and Pamlico River estuaries (Table 1; Figs. 17 and 18). Using the high spatial resolution capability of the MERIS chlorophyll data product, data were derived from channels, small creeks, and rivers not usually included in DWQ assessments. This additional information provided for a better understanding of the spatial impact of high chl *a* concentrations. In general, the MERIS data indicated there were 12 times between March 2006 and June 2009 when the 10/40 criterion was exceeded in the Neuse River estuary (Table 1). For the Pamlico River, the data indicated the 10/40 criterion had been exceeded 14 times during the same time period. The percentage of pixels that violated the criterion suggested that more hectares (ha) was impaired by chlorophyll *a* in



**Fig. 15.** Composites of MERIS derived chl  $a_{\text{ambient}}$  for the Neuse River Estuary from 2006 to 2009. The number ( $n$ ) of images composited is shown for each year. The distance scale is 20 km. Intended for color reproduction on the Web and in print.

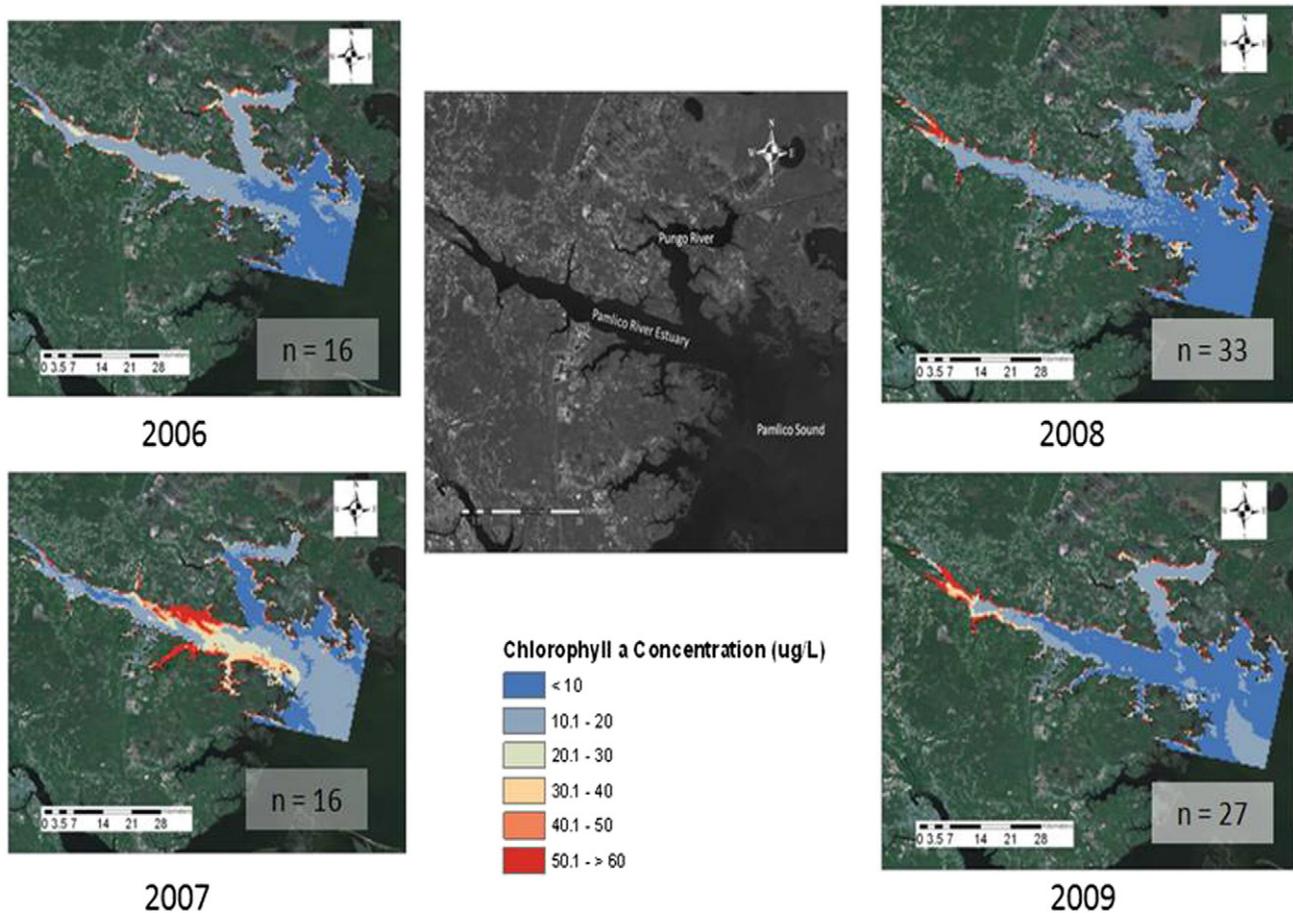
the Pamlico River estuary system than the Neuse River Estuary system (10,990 ha vs. 8801 ha; Table 1). The number of hectares impaired in the Neuse River Estuary by high chlorophyll  $a$  concentrations ranged from a minimum of 292 ha (on 7/28/2006) to a maximum of 13,963 ha (on 2/23/2007; Table 1; Fig. 17). The daily average for the NRE was 3712 ha. For the Pamlico River Estuary, the number of hectares impaired ranged from 630 ha (on 7/28/2006) to a maximum of 18,161 ha (on 1/29/2007; Fig. 18). The daily average for the PRE over the time period was estimated to be 4823 ha.

In the 2009 Neuse River Basin report, NCDWQ estimated that 21,811 ha in the Neuse River Estuary was impaired by chlorophyll during the 2002–2006 assessment period (NCDWQ, 2009). In comparison, with only 2006 to overlap, the MERIS chlorophyll data ( $n = 16$  images) indicated that a total of 58,098 ha was impaired by chl  $a$  concentrations greater than 40  $\mu\text{g/L}$  with a daily average of 3631 ha. When the area impaired is summed for periods of TMDL and Chl standard violations, the MERIS data indicated that a total of 105,624 ha was impacted by chlorophyll, with an average of 8801 ha (Table 1). In the 2010 Basin Report for the Pamlico Estuary, DWQ estimated that 11,735 ha was impaired. The MERIS-based assessment indicated that in total 142,554 ha was estimated to have been impaired from 2006 to 2009 during periods of TMDL and chl standard violations (Table 1). The average impaired area per image was 10,965 ha. The data also clearly indicated that seasonal variability played an important role in the mobilization, processing and delivery of nutrients to these estuaries during the later winter and spring season of each year. 2007 was an exceptional year as a wet 2006 winter and spring seasons resulted in more than twice the amount of impaired acreage compared to 2006, 2008, and 2009. The wet fall of 2006 was

followed by the beginning of a prolonged summer drought which significantly reduced the impaired area estimates.

### 3.8. Summary statistics of chlorophyll $a$ concentrations to support environmental compliance monitoring in estuaries for exceedances of nutrient criteria

In this section, the MERIS chl  $a$  product is used to evaluate which summary statistic of chl  $a$  (either sample mean, median, or 90th percentile values) would be most useful for determining violations of the 10/40 criterion and to support environmental compliance monitoring when compared to NC water quality standard. When mean and median chlorophyll values are plotted against time, the results showed that these statistics underestimated the number of estuarine acres which exceeded the chlorophyll standard. An examination of both datasets indicated that using these as criteria to identify exceedance, there were no values greater than the standard and both estuaries were in compliance with the 10/40 criterion from 2006 to 2009 (Figs. 19 and 20). This is clearly not the case based on the chlorophyll data product and the images presented previously. In comparison, the scatterplot of 90th percentile values, which represented the largest phytoplankton blooms, distinctly indicated that chl  $a$  threshold had been exceeded, probably in response to tropical storm Ernesto and the 2006 Nor'easter (Fig. 21). The 90th percentile plots also indicated the time sequence of bloom initiation, 10/40 criterion violation and the length of time it took for the system to return to pre-violation conditions.



**Fig. 16.** Composites of MERIS derived chl  $a_{\text{ambient}}$  for the Pamlico River Estuary from 2006 to 2009. The number (n) of images composited is shown for each year. The distance scale is 28 km. Intended for color reproduction on the Web and in print.

#### 4. Conclusions

The MERIS chl  $a$  data product was successfully used to conduct a retrospective analysis of the chlorophyll-based TMDL for total nitrogen which serves as the cornerstone of the nutrient management strategy for the Neuse and Pamlico River estuaries. This analysis indicated that

the TMDL standard for total nitrogen for the Neuse and Pamlico River estuaries, which is based on the NC chl  $a$  water quality standard, has not been met for the designated uses for the Neuse and Pamlico River estuaries due to large areas of impairment and numerous exceedances of the NC water quality standard at several time scales. The conclusion has been previously confirmed by others (e.g., NCDWQ, 2009, 2010a).

**Table 1**  
Dates when both the NC State Water Quality Standard and the 10/40 criterion were exceeded in the Neuse and Pamlico River estuaries, with the total and average number of area impaired by chlorophyll.

Date	Neuse River Estuary		Tar-Pamlico Estuary	
	Percentage of pixels that violate the 10/40 criterion	Impaired area (ha)	Percentage of pixels that violate the 10/40 criterion	Impaired area (ha)
3/4/2006	10.3	5274	<10	–
1/10/2007	<10	–	17.5	11,318
1/26/2007	12.5	4713	22.3	14,439
1/29/2007	16.5	8534	28.1	18,161
2/11/2007	19.7	11,102	15.4	9980
2/23/2007	27.1	13,963	26.3	16,992
2/24/2007	22.9	11,810	21.7	14,055
3/12/2007	15.0	7727	10.9	7066
3/18/2007	27.6	13,548	27.9	18,038
3/30/2007	24.6	12,671	13.2	8565
1/1/2009	9.2	4751	12.2	7904
2/5/2009	10.9	5636	10.9	7035
2/15/2009	11.4	5889	11.1	7166
4/23/2009	<10	–	10.2	6627
6/10/2009	<10	–	10.1	6520
Total		105,624		153,872
Average		8801		10,990

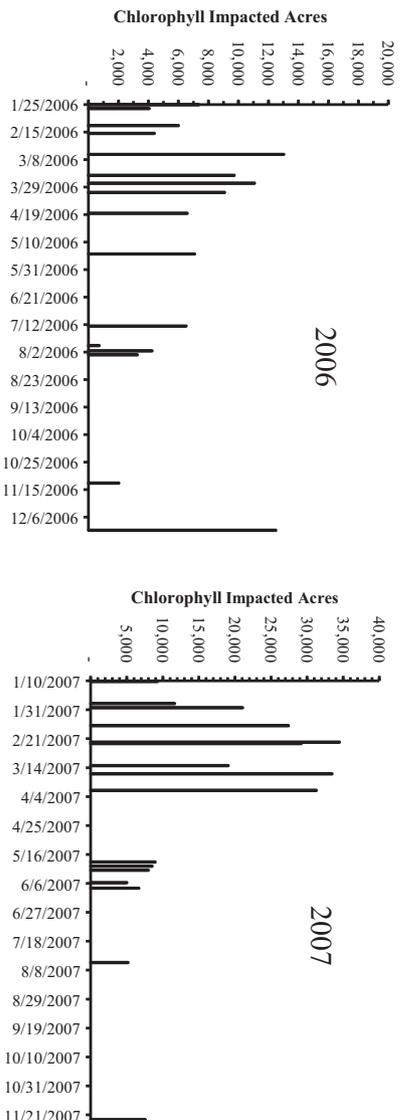


Fig. 17. Neuse River Estuary impaired acres due to chlorophyll  $a$  from 2006 to 2009 based on MERIS data. Note the scale change in 2007.

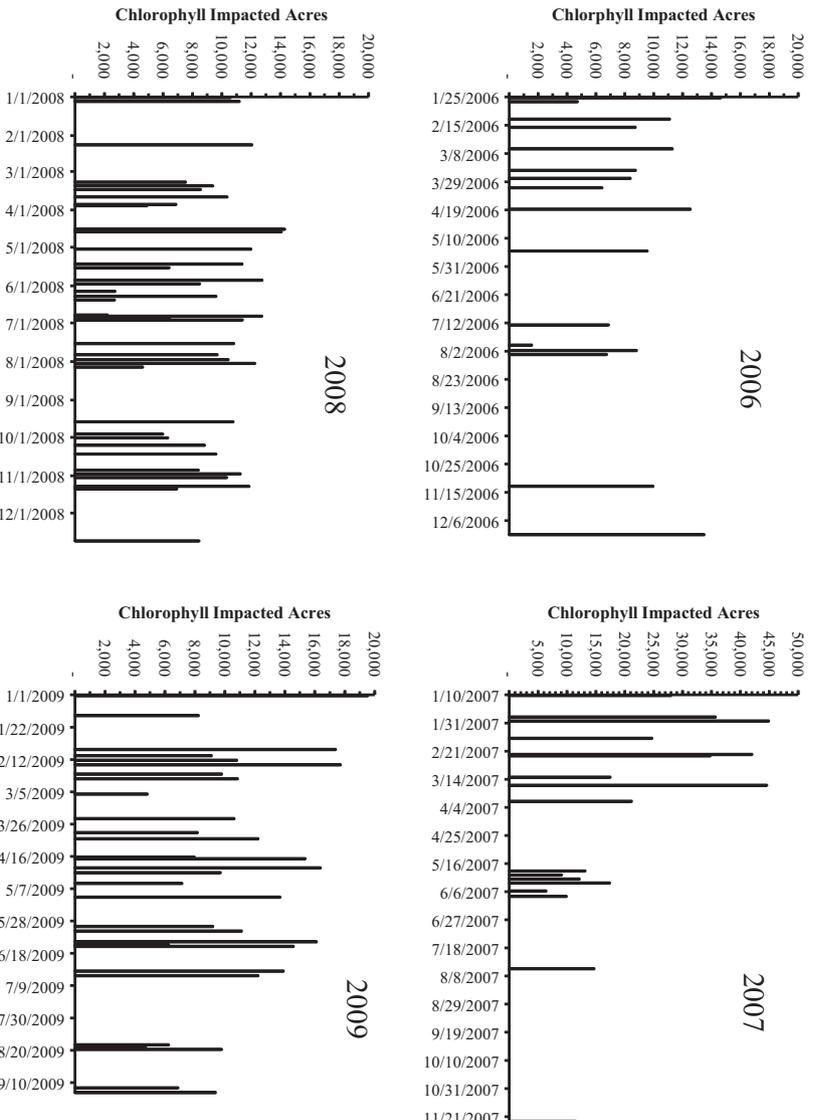


Fig. 18. Pamlico River Estuary impaired acres due to chlorophyll  $a$  from 2006 to 2009 based on MERIS data. Note the scale change for 2007.

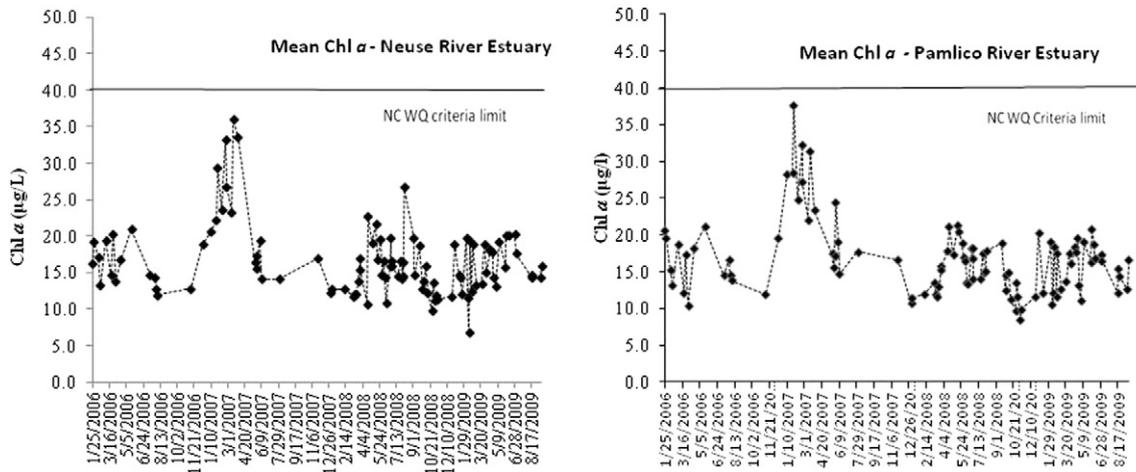


Fig. 19. Mean chlorophyll *a* estimates from 2006 to 2009 for the Neuse and Pamlico River estuaries.

The MERIS data indicated that whether these waters are viewed on a daily basis or over longer time periods there are large areas of these estuaries that routinely exceed the state water quality standard of 40 µg/L and which are not in compliance with the 10/40 criterion, even with the 30% nitrogen reduction strategy in effect. The high spatial resolution of the MERIS dataset allowed for observing creeks and streams that chronically exceed the standard and criterion as well as estimation of the amount of estuarine acreage impaired due to excess chlorophyll. It should be noted that the revisit period and spatial resolution of MERIS and other satellite sensing packages may not capture physical oceanographic processes such as cross-estuary sloshing or upwelling events which may greatly increase surface chlorophyll values, as well as periods of water quality standard violations, at local scales in the Neuse and Pamlico estuaries. When MERIS data coincided with NCDWQ field data, comparisons were made on the spatial distribution of impairment. The MERIS results indicated that the Pamlico estuary contained more impaired area than the Neuse estuary. For either estuary, the data indicated that on a daily basis tens of thousands of acres are impaired and when viewed on annual time scales, the number of impaired acres can increase by an order of magnitude. When these data are compared with estimates from DWQ there is the suggestion that point sampling methods employed in the field significantly underestimated the spatial extent of estuarine impairment. From the high temporal resolution of the data product, it was possible to create a time series of the evolution of a TMDL violation that lasted over several months in response to large-scale weather events as well as observe these

systems return to compliant conditions. This study also showed that the 90th percentile statistic is an effective indicator for monitoring remotely sensed chl *a* concentrations in the context of observing water quality exceedances and violations of TMDL standard and to support environmental compliance.

The MERIS sensor data provided additional information to the measurement in space and time of phytoplankton abundance in response to changes in hydrology and to nutrient loading. These data clearly illustrated the occurrence of extensive and frequent periods of chl *a* standard and 10/40 criterion violations. Using this information, the frequency of these violations can be quantified and used to revisit the percent reduction in TN needed to bring the Neuse and Pamlico River estuaries into compliance with the 10/40 criterion. While data comparisons between MERIS derived Chl *a* and DWQ in-water measurements showed differences, routinely collected remotely sensed data can be used to quantify the temporal and spatial occurrence of exceedances and violations as well as compliment and add value to NCDENR four year basin reports for the Neuse and Pamlico estuaries by providing more comprehensive information. Additionally, data from satellite platforms can supplement NCDWQ monitoring activities on daily, monthly and annual time periods by identifying “hot spots” where additional sources of nitrogen may be added to the system from streams and creeks, as well as further understanding of the biological and hydrological characteristics of these aquatic ecosystems and the environmental impacts of the land-use practices within the surrounding environment.

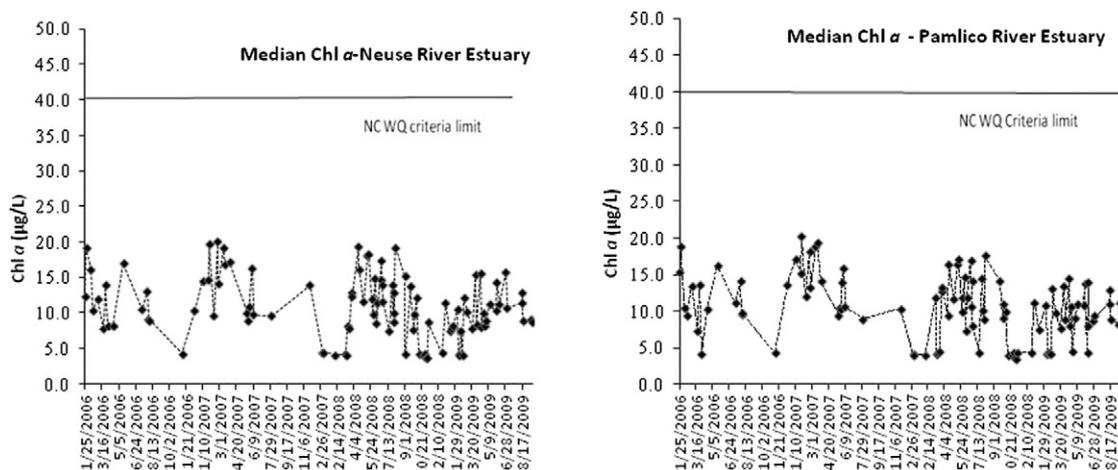


Fig. 20. Median chlorophyll *a* estimates from 2006 to 2009 for the Neuse and Pamlico River estuaries.

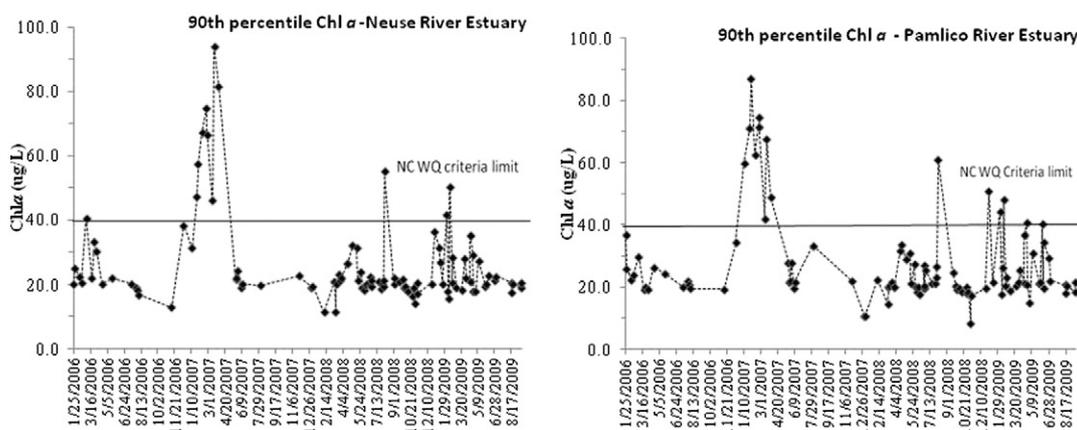


Fig. 21. 90th percentile chlorophyll estimates from 2006 to 2009 for the Neuse and Pamlico River estuaries.

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**References**

APNEP (P). The Albemarle–Pamlico Estuary. Albemarle–Pamlico National Estuary Partnership. <http://portal.ncdenr.org/web/apnep/our-estuaries>

Arar, E. J., & Collins, G. B. (1997). Method 445.0 *in vitro* determination of chlorophyll *a* and pheophytin *a* in marine and freshwater algae by fluorescence. *US Environmental Protection Agency EPA/600/R-97/072*.

Batiuk, R. A., et al. (2000). Chesapeake Bay submerged aquatic vegetation water quality and habitat-based requirements and restoration targets: A second technical synthesis. *EPA Chesapeake Bay Program Report, Annapolis, MD*.

Borsuk, M., Clemen, R., Maguire, L., & Reckhow, K. (2001). Stakeholder values and scientific modeling in the Neuse River Watershed. *Group Decision and Negotiation, 10*, 355–373.

Borsuk, M., Stow, C. A., & Reckhow, K. H. (2003). Integrated approach to total maximum daily load development for Neuse River Estuary using Bayesian Probability Network Model (Neu-BERN). *Journal of Water Resources Planning and Management-ASCE, 271*–282. [http://dx.doi.org/10.1061/\(ASCE\)0733-9496\(2003\)129:4\(271\)](http://dx.doi.org/10.1061/(ASCE)0733-9496(2003)129:4(271)).

Dodd, R. C., Cunningham, P. A., Curry, R. J., & Stichter, S. J. (1993). *Watershed Planning in the Albemarle–Pamlico Estuarine System, Report No. 93-01*. Research Triangle Park, NC: Research Triangle Institute. Department of the Environment, Health and Natural Resources.

Doerffer, R., & Schiller, H. (2007). The MERIS Case 2 water algorithm. *International Journal of Remote Sensing, 28*, 517–535. <http://dx.doi.org/10.1080/01431160600821127>.

Harned, D. A., & Davenport, M. S. (1990). Water-quality trends and basin activities and characteristics for the Albemarle–Pamlico estuarine system, North Carolina and Virginia. *USGS Open-File Report 90-398* (164 pp.).

Karaska, M. A., Huguein, R. L., Beacham, J. L., Wang, M. -H., Jensen, J. R., & Kaufmann, R. S. (2004, January). AVIRIS measurements of chlorophyll, suspended minerals, dissolved organic carbon, and turbidity in the Neuse River, North Carolina. *Photogrammetric Engineering & Remote Sensing, 70*(1).

Khorrarn, S., & Cheshire, H. M. (1985). Remote sensing of water quality in the Neuse River Estuary, North Carolina. *Photogrammetric Engineering & Remote Sensing, 51*, 329–341.

Luetlich, R. A., Jr., McNinch, J. E., Paerl, H. W., Peterson, C. H., Wells, J. T., Alperin, M., et al. (2000). Neuse River Estuary modeling and monitoring project stage 1: Hydrography

and circulation, water column nutrients and productivity, sedimentary processes and benthic-coupling. *Report UNC-WRRI-2000-325B*. Raleigh, NC: Water Resources Research Institute of the University of North Carolina (172 pp.).

Lunetta, R. S., Knight, J. F., Paerl, H. W., Streicher, J. J., Peierls, B. L., Gallo, T., et al. (2009). Measurement of water color using AVIRIS imagery to assess the potential for an operational monitoring capability in the Pamlico Sound Estuary, USA. *International Journal of Remote Sensing, 30*, 3291–3314. <http://dx.doi.org/10.1080/01431160802552801>.

MAIA (2002). Mid-Atlantic Integrated Assessment (MAIA) Estuaries 1997–98. *Summary report; environmental conditions in the Mid-Atlantic Estuaries. EPA/620/R-02/003*. US Environmental Protection Agency.

Mobley, C. D. (1994). *Light and water: Radiative transfer in natural waters*. San Diego: Academic Press (592 pp.).

NC Drought Management Advisory Council (2007). *Drought Management Advisory Council – Activities report*. Raleigh, NC: North Carolina Division of Water Resources, North Carolina Department of Environment and Natural Resources.

NCDEM (1989). *Tar–Pamlico River basin nutrient sensitive waters designation and nutrient management strategy*. Water Quality Section, North Carolina Division of Environmental Management.

NCDENR (2001). *Phase II of the total maximum daily load for total nitrogen to the Neuse River Estuary, North Carolina–Neuse River Basin*. North Carolina Department of Environment and Natural Resources (68 pg.).

NCDWQ (2009, July). *Final Neuse River Basinwide water quality plan*. Raleigh, NC: North Carolina Department of Water Quality, North Carolina Department of Environment and Natural Resources.

NCDWQ (2010a). *Tar–Pamlico River Basinwide water quality management plan*. Raleigh, NC: North Carolina Department of Water Quality, North Carolina Department of Environment and Natural Resources.

NCDWQ (2010b). *Nutrient sensitive water strategy. Tar–Pamlico River Basin Plan. Chapter 6*. Raleigh, NC: North Carolina Department of Water Quality, North Carolina Department of Environment and Natural Resources.

Paerl, H. W. (2008, July). FerryMon, Ferry-based monitoring and assessment of water quality for North Carolina's Pamlico Sound. *WRRI Report No. 387*. Raleigh, NC: UNC Water Resources Research Institute (64 pp.).

Paerl, H. W. (2009). Controlling eutrophication along the freshwater–marine continuum: dual nutrient (N and P) reductions are essential. *Estuaries and Coasts, 32*, 593–601.

Paerl, H. W., Mallin, M. A., Rudek, J., & Bates, P. W. (1990, December). The potential for eutrophication and nuisance algal blooms in the Lower Neuse River Estuary. *Albemarle–Pamlico Estuarine study-supported Project. Project No. 90-15 and EPA-CE 00470601, Final Report*.

Paerl, H. W., Rossignol, K. L., Hall, N. S., Guajardo, R., Joyner, A. R., Peierls, B. L., et al. (2009). FerryMon: ferry-based monitoring and assessment of human and climatically-driven environmental change in the Pamlico Sound System, North Carolina, USA. *Environmental Science and Technology, 43*, 7609–7613.

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*, 485–497.

Peierls, B. L., Hall, N. S., & Paerl, H. W. (2012). Non-monotonic responses of phytoplankton biomass accumulation to hydrologic variability: A comparison of two coastal plain North Carolina estuaries. *Estuaries and Coasts, 35*, 1376–1392.

Roth, D. (2007). *Rainfall summary for Hurricane Ernesto*. College Park, Maryland: Hydrometeorological Prediction Center. National Weather Service National Centers for Environmental Prediction, Weather Prediction Center.

Sokoletsky, L. G., Lunetta, R. S., Wetz, M. S., & Paerl, H. W. (2011). MERIS retrieval of water quality components in the turbid Albemarle–Pamlico Sound Estuary, USA. *Remote Sensing, 3*, 684–707. <http://dx.doi.org/10.3390/rs3040684>.

Spruill, T. B., & Bratton, J. F. (2008). *Estimation of groundwater and nutrient fluxes to the Neuse River Estuary, North Carolina. USGS Staff-Published Research. Paper 288* (<http://digitalcommons.unl.edu/usgsstaffpub/288>).

Stanley, D. W. (1988). Historical trends in nutrient loading to the Neuse River Estuary, NC. In W. Lyke, & T. Hoban (Eds.), *Proceedings of the American Water Resources Association*

- Symposium on Coastal Water Resources. Tech. Pub. Ser.* (pp. 155–164). Bethesda, MD: AWRA.
- Stow, C. A., Borsuk, M. E., & Stanley, W. (2001). Long-term changes in watershed nutrient inputs and riverine exports in the Neuse River, North Carolina. *Water Research*, 35, 1489–1499.
- Stow, C. A., Roessler, C., Borsuk, M. E., Bowen, J. D., & Reckow, K. H. (2003). Comparison of estuarine water quality models for total maximum daily load development in Neuse River Estuary. *Journal of Water Resources Planning and Management-ASCE*, 129(4). [http://dx.doi.org/10.1061/\(ASCE\)0733-9496\(2003\)129:4\(307\)](http://dx.doi.org/10.1061/(ASCE)0733-9496(2003)129:4(307)).
- Strobel, C. J., & Heitmuller, T. (2001). National coastal assessment field operations manual. *EPA/620/R-01/003*. US Environmental Protection Agency.
- Tesoriero, A. J., Duff, J. H., Saad, D. A., Spahr, N. E., & Wolock, D. M. (2013). Vulnerability of streams to legacy nitrate sources. *Environmental Science and Technology*, 47, 3623–3629. <http://dx.doi.org/10.1021/es305026x>.
- Tester, P., Varnam, S. M., Culver, M. E., Eslinger, D. L., Stumpf, R. P., Swift, R. N., et al. (2003). Airborne detection of ecosystem responses to an extreme event: Phytoplankton displacement and abundance after hurricane induced flooding in the Pamlico–Albemarle Sound System, North Carolina. *Estuaries*, 26(5), 1353–1364.
- USEPA (1993). *TMDL case study: Tar–Pamlico Basin, North Carolina*. Office of Water (WH-553), EPA841-F-93-010 (7 pg.).
- Vähätalo, A., Wetzel, R., & Paerl, H. (2005). Light absorption by phytoplankton and chromophoric dissolved organic matter in the drainage basin and estuary of the Neuse River, North Carolina. *Freshwater Biology*, 50, 477–493. <http://dx.doi.org/10.1111/j.1365-2427.2004.01335.x>.
- Wetz, M. S., Hutchinson, E. A., Lunetta, R. S., Paerl, H. W., & Taylor, J. C. (2011). Severe droughts reduce estuarine primary productivity with cascading effects on higher trophic levels. *Limnology and Oceanography*, 56(2), 627–638.
- WRRRI (2001). *The chlorophyll a standard: A primer*. Raleigh, NC: UNC Water Resources Research Institute (<http://www2.ncsu.edu/ncsu/CIL/WRRRI/>).