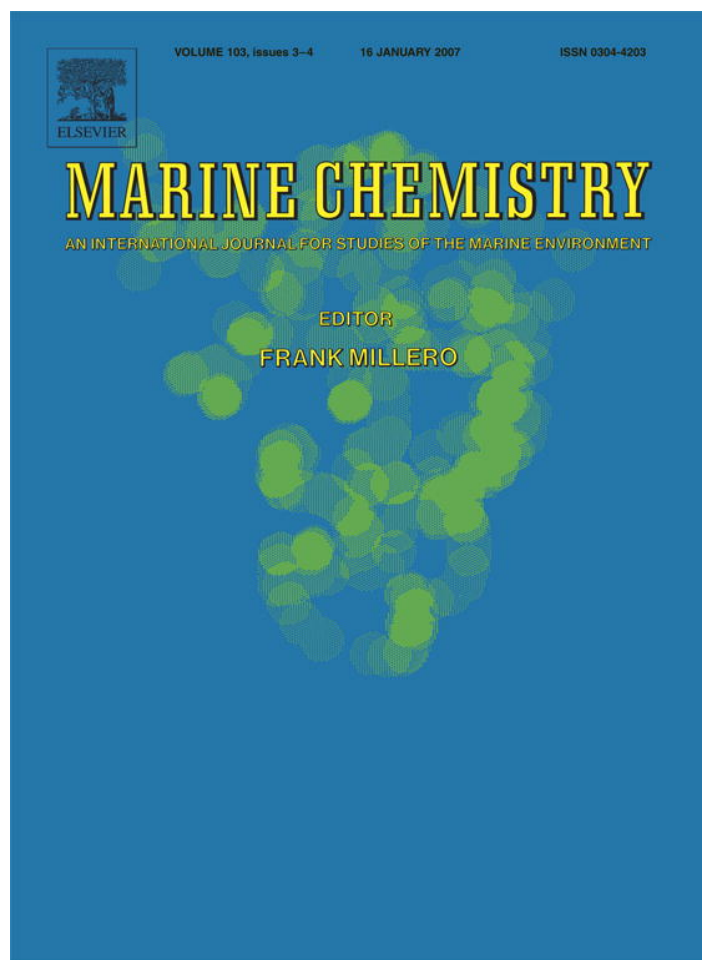


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Nitrogen and phosphorus species in the coastal and shelf waters of Southeastern North Carolina, Mid-Atlantic U.S. coast

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Abstract

The diversity of small-scale wetlands, high salinity tidal creeks, salt marshes, estuaries, and a wide and shallow shelf with the Gulf Stream close to the break makes the coastal zone of south-eastern North Carolina (U.S.) a natural laboratory for the study of the cycling of nitrogen (N) and phosphorus (P) in coastal and shelf waters. We assessed the summer concentrations, forms, and ratios for each N (total dissolved N, nitrate+nitrite, ammonium and dissolved organic N) and P (total dissolved P, *o*-phosphate and dissolved organic P) pool as these nutrients travel from tidal creeks, salt marshes and two large estuaries to Long and Onslow Bays. Additionally, we measured ancillary physical (temperature, salinity and turbidity) and chemical (dissolved oxygen, chlorophyll *a* and pH) water properties. Highest concentrations of all individual N and P compounds were found in the upper parts of each tributary and were attributed to loads from agricultural and urban sources to the coastal watersheds, continuing downstream to receiving estuaries. In all areas, dissolved organic N and P species were predominant constituents of the total dissolved N and P pools (64–97% and 56–93%, respectively). The lower parts of estuaries and surface shelf waters were characterized by oceanic surface values, indicating removal of N and P downstream in all tributaries. The different watershed and hydrological characteristics also determined the different speciation of N and P pools in each estuary. Despite a high level of anthropogenic pressure on the uppermost coastal waters, there is self-regulation in this coastal ecosystem with respect to human perturbations; i.e. significant amounts of the N and P load are retained within estuarine and nearshore waters without reaching the shelf.

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1. Introduction

It has become evident over the last 50 years that most terrestrial and aquatic environments are changing under the increasing pressure of human activities: fossil fuel burning, changes in land use, application of organic and

inorganic fertilizers to agricultural croplands, and loading of municipal and industrial sewage to coastal environments (Mackenzie et al., 2002). These changes are responsible for major reorganization of essential global biogeochemical cycles. The major biogeochemical cycles of the elements carbon (C), nitrogen (N) and phosphorus (P) are coupled on the global scale. However, to fully understand the global biogeochemical cycles of biologically important elements such as carbon, it is necessary to

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know the processes controlling the sources and sinks of N and P in the terrestrial, atmospheric and oceanic ecosystems.

From this aspect, the coastal zone of the oceans is of special interest as the area of anthropogenic pressure release *via* gaseous, liquid and solid emission of organic and inorganic C, N and P. Riverine and atmospheric transport link the terrestrial to the coastal ocean realm; gas exchange and accumulation are the process links with the atmosphere; advective transport of water, dissolved and particulate matter link it with the open ocean; and deposition and burial of organic and inorganic organic material (OM) are its links with the sediment domain (Rabouille et al., 2001). There are indications that the global fluxes of C, N and P by rivers to the coastal ocean have increased over time (Cole et al., 1993; Howarth et al., 1996; Meybeck, 1993). The enhanced discharge of inorganic N and P to coastal waters *via* rivers and the atmosphere (N only) has led to increased new production (Burkholder, 2001), burial of organic C in marine sediments (Smith and Hollibaugh, 1993) and enhanced denitrification (Koike and Sorensen, 1988). On local and regional scales, these increased inputs to coastal marine waters have led to problems of eutrophication and degradation of coastal marine ecosystems (De Jonge et al., 1994). Prolonged and intensive use of inorganic fertilizers in agriculture, changes in land use patterns, deforestation, and discharge of industrial and municipal waste have all contributed to the eutrophication of river water and the coastal ocean on a global scale (Rabouille et al., 2001). As a result, eutrophication in some estuaries has led to the loss of valuable seagrass (Burkholder et al., 1992) and reef habitats (Lapointe, 1997), and affects valuable shell- and fin-fish stocks (Valiela and Bowen, 2002 and references therein).

To understand the role of the coastal zone in biogeochemical cycles of C, N and P, we need to know local processes that control the cycling of these elements on smaller scales. From this point of view, wetlands, tidal creeks, and salt marshes are areas that are well suited for study, due to their location at the terrestrial/oceanic interface. The major objective of this paper is to draw the attention of marine chemists to the 'inner' coastal zone, which is influenced by both natural and considerable anthropogenic pressures. We have evaluated the partitioning of riverine and marine N and P between various reservoirs in the coastal and shelf environments. The concentrations, forms, and ratios for mineral and organic N and P components have been assessed as these nutrients traverse from upstream in tidal creeks, salt marshes and two large estuaries to the

continental shelf of Long and Onslow Bays, Mid-Atlantic U.S. coast.

1.1. Study area

The study area includes the diverse collection of estuaries, wetlands and salt marshes along the southeastern North Carolina coast, and the continental shelf waters eastward to the Gulf Stream. The most significant estuaries are the lagoonal New River Estuary and, 65 km to the south, the Cape Fear River Estuary, which drains the largest watershed in North Carolina (Mallin et al., 2000). This coastal region hosts a maze of oligohaline to euhaline tidal creek estuaries ranging from 1 to 10 km in length, and up to 2.5 m in depth at high tide. Most of this coastline is sheltered from the open ocean by barrier islands, which play a major role in hydrological and biological estuarine processes. Tidal creeks drain uplands in various stages of development, and feed into the Atlantic Intra-Coastal Waterway (AICWW), which is connected with the adjacent shelf water by a series of narrow inlets within the extensive chain of barrier islands. These relatively small estuarine areas are often less than 1–2 km in width but extend 10–20 km between inlets. They have extensive intertidal regions, salt marshes (often greater than 50–70% of the total area), relatively high salinities (often reaching 35–37), and are well flushed (Mallin et al., 2000; 2004). Tidal range in this region is about 1.1 m (Dame et al., 2000).

The lower Cape Fear River system is not constrained by barrier islands and discharges directly to Long Bay. Its principal channel is the Cape Fear River, a sixth-order stream (on a scale from first-order small tributaries to twelfth-order large rivers) that arises in the Piedmont near Greensboro, NC (Mallin et al., 1999). The lower river is joined by two fifth-order blackwater tributaries, the Black and Northeast Cape Fear Rivers, which originate in the coastal plain. These systems feed the Cape Fear River Estuary, a system 72 km long that flows unimpeded into the Atlantic Ocean. Much of this estuary is <3.0 m deep except for a 14 m deep ship channel extending throughout the estuary.

From the barrier islands, the continental shelf gradually deepens to approximately 100 m at the shelf break where the shelf and Gulf Stream waters interact (Mallin et al., 2000). Frictional forcing by the Gulf Stream drives the predominantly counter-clockwise circulation in Onslow and Long Bays. Filaments of offshore water sometimes move inshore along the south side of the shoals seaward of Cape Fear. Topographic features, a rise in continental slope, and wind forcing drive Gulf Stream meanders up to 30–40 km seaward of

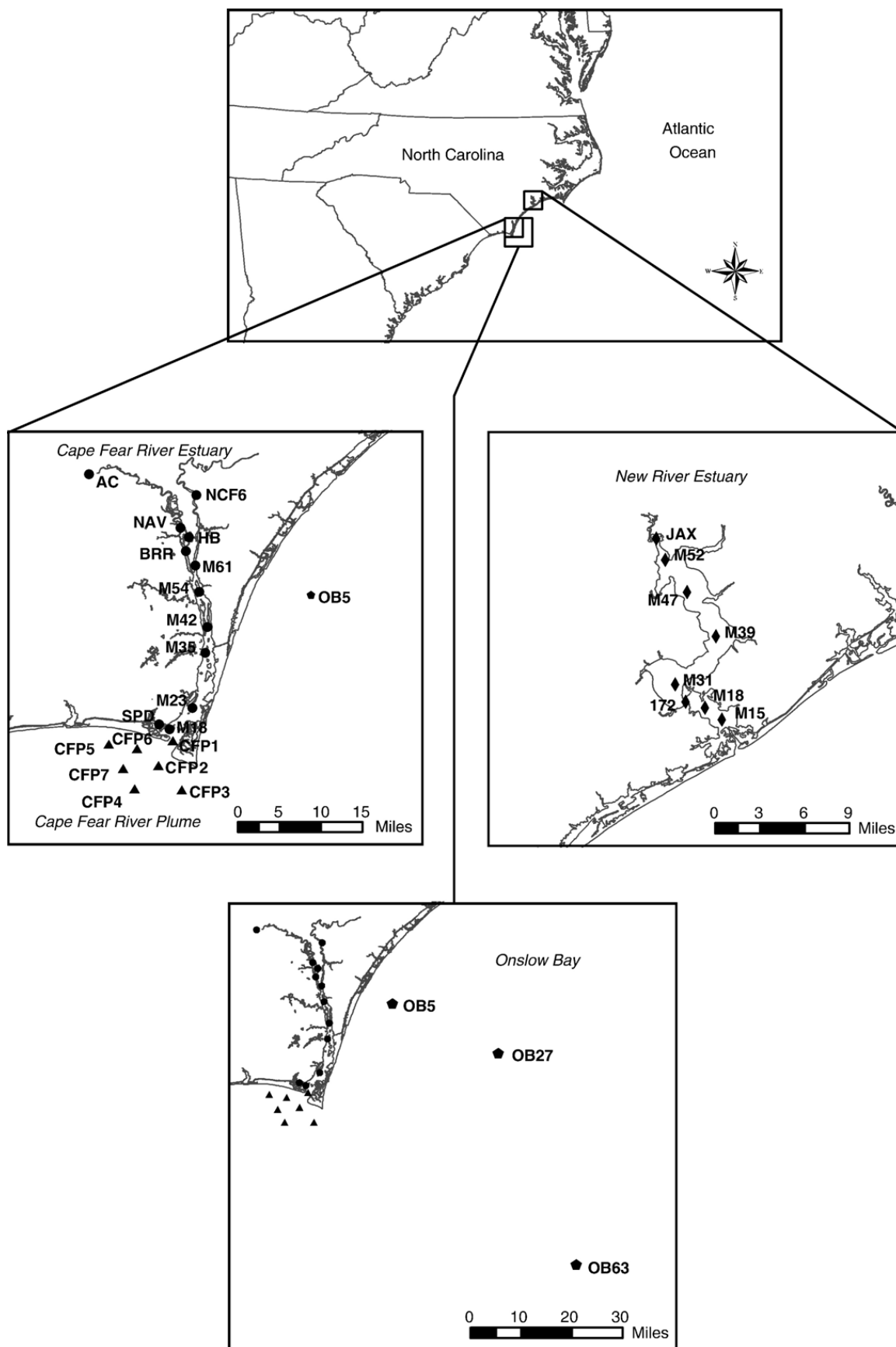


Fig. 1. Location of sampling sites along the coast of southeastern North Carolina, USA. Includes the Cape Fear River estuary and plume with tidal creeks (not individually labelled) depicted along the ocean shore (left), the New River estuary (right), and Onslow Bay (bottom).

the shelf break or onto the shelf itself (Pietrafesa et al., 1985). Intrusions typically reach the mid-shelf, but may reach as near as 10 km from the shore (Atkinson et al., 1980). Meanders are also associated with shelf-edge upwelling, which can advect nutrient-enriched slope water onto the shelf. Upwelled nutrients are a significant portion of total nutrients entering the shelf ecosystem (Atkinson, 1985). Wind forcing, particularly associated with storms, can drive significant flows shoreward (Pietrafesa and Janowitz, 1988).

2. Materials and methods

2.1. Field sampling

Samples were collected in several tidal creeks (New Hanover County, NC), the Cape Fear and the New River estuaries, the Cape Fear River plume (Long Bay) and in Onslow Bay in 2002 (Fig. 1). It has been previously demonstrated that in the Cape Fear River Estuary there were not statistically significant differences between surface and bottom nutrient and chlorophyll *a* (Chl *a*) concentrations, with the exception of total dissolved P (TDP) and sometimes ammonium (Mallin et al., 1996). Thus, samples for nutrient analyses were collected from a depth of about 20 cm between high and mid-ebb tide in pre-washed plastic bottles (Nalgene®) and frozen prior to analysis (under the auspices of several programs). Since 2000, the University of North Carolina at Wilmington Coastal Ocean Research and Monitoring Program (CORMP) has collected data at seven stations located in and near the plume of the Cape Fear River where it enters the Atlantic Ocean (Mallin et al., 2005a). This program also obtains physical, chemical and biological data at several stations along a transect in Onslow Bay including the following sampled sites: OB5 (8 km offshore), OB27 (45 km offshore), and OB63 (100 km offshore). Samples from eight tidal creeks were collected within the framework of the New Hanover County Tidal Creeks Program, conducted since 1994 for a suite of physical, biological, and chemical parameters (Mallin et al., 2004). Under the auspices of the Lower Cape Fear River Program, running since 1996 (Mallin et al., 1999), samples were also taken at twelve stations located in the Cape Fear River watershed, including a number in the estuary, tidal river proper, and in the two most important tributaries, the Black and Northeast Cape Fear Rivers. Eight stations were also sampled in the northernmost estuary studied, the New River Estuary (Mallin et al., 2005b). Much of the data presented here are available on line at <http://www.uncwil.edu/cmsr/aquaticceology/TidalCreeks/>, and

<http://www.uncwil.edu/cmsr/aquaticceology/lcfrp/>, <http://www.cormp.org>.

2.2. Physical, chemical and biological properties analyses

Water temperature, conductivity, dissolved oxygen (DO), turbidity and pH data were collected at each station using a YSI 6920 Multi-Parameter Water Quality Monitor connected to a YSI 610D display unit (Table 1). Triplicate water samples for Chl *a* analysis were filtered through Millipore or Gelman A/E glass-fiber filters (nominal pore size 1 μm). Chl *a* was analyzed three times in the same sample using a fluorometry method (Welschmeyer, 1994). The analytical accuracy of Chl *a* analysis was within 8%.

2.3. N and P species analyses

All analyses were made with a two system Bran+Luebbe Continuous Flow AutoAnalyzer III (CFA III) for simultaneous analysis of nitrate, ammonium and *o*-phosphate (three channels of the system one), and TDN and TDP (two channels of the system two) in a single sample. The techniques are based on the Technicon® methodologies for nitrate (Technicon, 1972) and *o*-phosphate analyses in seawater (Technicon, 1973). Ammonium was analyzed by two methods: (1) manually by the modified spectrophotometric method (Parsons et al., 1984), and (2) with the CFA III using a

Table 1

The overall performance of nutrient analyses with the Bran+Luebbe CFA III (all in μM); SD — standard deviation, CV — coefficient of variation, and YSI 6920 Multi-Parameter Water Quality Monitor connected to a YSI 610D display unit

CFA III analyses				
Parameter	Detection limit	Precision	SD	CV, %
Nitrate	0.009	0.03	0.9	9.4
Ammonium	0.050	0.05	0.28*	25.7*
			0.07	8.6
<i>O</i> -phosphate	0.006	0.02	0.01	4.5
DON	1.230	0.38	0.37	4.0
DOP	0.051	0.02	0.02	4.3
Multi-Parameter Water Quality Monitor				
			Accuracy	Resolution
T, °C			±0.15	0.01
S			±1%	0.01
DO, μmol kg ⁻¹			±13	
Turbidity			±5%	0.1 NTU
pH, units			±0.2	0.001

*-Analyzed manually by the spectrophotometric method (Parsons et al., 1984).

high-sensitivity modification of the Slawyk and MacIsaac (1972) method (Szmant et al., 1990). TDN and TDP were analyzed with the CFA III by the photo-chemical oxidation method (Dafner and Szmant, in preparation). DON and DOP were calculated as the difference between total and mineral N and P species.

Specifications for all chemical analyses, including precision, accuracy, and detection limits are provided in Table 1. The limits of detection were estimated as three times the SD of lower concentrations measured in all samples (Taylor, 1990). The precision of all methods was evaluated based on the SD and coefficient of variation (CV in %) obtained for the analyses of all natural freshwater and seawater samples. The SD for the

DON and DOP concentrations was calculated by propagating the error according to Bevington (1969). All regressions are reported using model II geometric mean regression parameters (Sokal and Rohlf, 1995).

3. Results

3.1. Spatial heterogeneities of N and P species

The overview of all data, presented in Tables 2 to 4, shows that almost all nutrient concentrations decrease significantly from inshore in the direction of the open ocean, with minimum concentrations at the shelf close to the Gulf Stream. All areas with high values of TDN

Table 2

Temperature (°C), salinity, dissolved oxygen, apparent oxygen utilization (AOU; both in $\mu\text{mol kg}^{-1}$), DO saturation (%), Chl *a* ($\mu\text{g l}^{-1}$), turbidity (Turb.; NTU), pH, N and P species (μM) concentrations in tidal creeks, the Cape Fear River and New River estuaries

Station	T	S	O ₂	AOU	O ₂	Chl <i>a</i>	Turb.	pH	NH ₄ ⁺	NO ₃ ⁻	TDN	DON	HPO ₄ ²⁻	TDP	DOP
<i>Tidal creeks, July 2002</i>															
PC-BDDS	30.3	33.6	168	23	88	7.5	10	7.8	1.28	0.15	14.91	13.49	0.24	0.60	0.36
PC-BDUS	30.9	25.5	182	17	91	20.1	12	7.6	1.17	0.14	19.59	18.29	0.18	0.72	0.54
FC-17	27.6	30.2	162	41	80	7.1	24	7.4	9.34	0.85	18.76	8.58	0.20	0.71	0.51
BNC-RR	28.9	16.8	167	50	77	22.3	34	7.2	1.01	18.15	46.47	27.31	0.19	1.87	0.68
MOT-RR	26.8	15.8	127	99	56	20.0	18	7.5	0.71	2.53	31.72	28.48	0.28	0.84	0.57
WC-MLR	28.1	27.6	147	58	72	9.4	17	7.5	3.12	1.10	31.64	27.42	0.91	1.50	0.59
SB-PGR	32.0	11.8	302	-89	142	36.4	19	8.2	1.51	0.38	58.32	56.44	1.93	4.98	3.05
NB-GLR	33.0	3.4	329	-108	149	27.1	17	8.2	3.54	0.24	21.03	17.25	0.36	2.48	2.12
BC-SB	23.6	2.5	188	73	72	54.7	23	7.0	1.77	0.19	32.13	30.18	0.80	1.82	1.03
BC-NB	27.2	15.6	115	110	51	20.8	17	7.1	1.39	7.48	39.02	30.15	0.25	0.88	0.64
HW-GP	32.2	2.1	263	-38	117	15.2	13	7.9	1.39	0.15	32.45	30.91	0.44	1.16	0.72
<i>Cape Fear River Estuary, June 2002</i>															
SPD	27.8	34.8	159	38	81	3.0	10	7.6	1.14	0.36	21.10	19.60	0.32	1.16	0.84
M18	26.6	33.6	199	4	98	2.2	5	8.0	1.43	0.36	16.58	14.80	0.32	0.91	0.59
M23	26.8	31.6	202	3	99	2.9	5	8.0	1.43	0.36	19.31	17.52	0.36	1.13	0.96
M35	27.2	24.4	246	-34	116	12.6	7	8.0	1.43	0.36	32.26	30.47	0.48	1.76	1.28
M42	27.2	22.6	262	-47	122	16.4	9	8.1	1.43	3.57	33.39	28.39	0.26	1.72	1.46
M54	27.2	20.0	228	-10	105	12.1	8	7.8	2.86	10.71	44.57	31.00	0.29	2.06	1.77
M61	27.3	17.7	201	20	91	9.4	9	7.6	7.14	15.71	40.63	17.77	0.90	1.94	1.04
BRR	26.8	13.3	180	50	78	8.7	11	7.3	7.14	24.29	61.81	30.38	1.32	2.47	1.15
HB	27.0	9.7	174	60	74	6.8	10	7.3	8.57	32.14	75.15	34.44	1.87	3.19	1.32
NCF6	27.5	8.2	190	44	81	22.3	17	7.1	2.86	17.14	52.99	32.99	1.26	2.23	0.97
NAV	26.7	6.0	153	88	63	5.3	14	7.1	8.57	55.00	80.19	16.62	2.36	3.21	0.85
AC	27.8	0.2	238	7	97	0.9	12	7.1	46.43	55.00	139.22	37.79	5.32	5.89	0.57
<i>New River Estuary, May 2002</i>															
M15	19.5	36.9	222	2	99	1.4	9	8.0	0.74	0.13	11.62	10.76	0.37	0.65	0.28
M18	18.8	33.0	223	10	96	2.4	6	8.0	0.85	0.08	19.45	18.52	0.58	0.92	0.34
172	18.7	28.8	230	11	96	4.3	7	7.9	0.93	0.09	29.66	28.64	0.86	1.35	0.49
M31	18.5	26.3	245	-0.1	100	6.6	6	8.0	0.70	0.08	38.53	37.75	1.02	1.88	0.86
M39	18.8	19.9	256	-1	101	5.2	7	8.0	0.58	0.06	41.23	40.59	0.87	1.49	0.62
M47	19.1	17.5	262	-5	102	2.5	3	8.0	0.81	0.06	41.79	40.91	0.73	1.44	0.73
M52	19.1	14.4	260	3	99	3.7	6	8.0	0.78	0.07	45.60	44.76	1.07	1.61	0.54
Jax	19.7	12.0	263	0.2	100	5.9	5	8.0	0.85	0.13	49.63	48.64	1.62	2.08	0.46

Locations of tidal creek sampling sites: Pages Creek (PC-BDUS, PC-BDDS); Futch Creek (FC-17); Barnards Creek (BNC-RR); Motts Creek (MOT-RR); Whiskey Creek (WC-MLR); Hewletts Creek (SB-PGR, NB-GLR); Bradley Creek (BC-SB; BC-NB); Howe Creek (HW-GP).

Table 3

Temperature (°C), salinity, dissolved oxygen, apparent oxygen utilization (AOU; both in $\mu\text{mol kg}^{-1}$), DO saturation (%), Chl *a* ($\mu\text{g l}^{-1}$), turbidity (Turb.; NTU), pH, N and P species (μM) concentrations in the Cape Fear River plume in April and July, 2002

Station	T	S	O ₂	AOU	O ₂	Chl	Turb.	pH	NH ₄ ⁺	NO ₃ ⁻	TDN	DON	HPO ₄ ²⁻	TDP	DOP
<i>April, 2002</i>															
CFP1	21.3	31.6	226	-4	102	2.6	14	8.0	0.21	1.68	18.42	16.53	0.16	1.09	0.93
CFP2	21.1	33.7	223	-1	101	2.5	13	8.0	0.21	0.88	13.65	12.56	0.16	1.01	0.85
CFP3	20.7	35.1	238	-16	107	0.8	5	8.1	0.05	0.26	9.81	9.55	0.11	0.56	0.45
CFP4	20.9	35.0	238	-17	108	1.2	4	8.1	0.05	0.30	7.87	7.57	0.11	0.51	0.40
CFP5	21.9	33.5	238	-21	110	0.8	5	8.1	0.05	0.24	9.29	9.05	0.11	0.50	0.39
CFP6	21.7	34.3	241	-23	110	2.3	5	8.1	0.57	0.31	10.53	9.65	0.12	0.61	0.49
CFP7	21.6	34.4	235	-17	108	1.0	4	8.1	0.05	0.24	9.15	8.90	0.10	0.54	0.43
<i>July, 2002</i>															
CFP1	30.1	33.9	177	14	93	2.6	6	8.0	1.14	0.58	16.80	15.08	0.24	1.11	0.87
CFP2	30.0	34.6	180	10	95	2.5	5	8.1	0.79	0.30	14.87	13.79	0.20	1.06	0.86
CFP3	30.3	35.2	199	-10	105	1.1	3	8.1	1.71	0.22	10.50	8.56	0.15	0.62	0.47
CFP4	29.5	35.6	195	-5	102	1.1	1	8.2	1.36	0.19	8.98	7.44	0.11	0.52	0.41
CFP5	29.7	35.3	192	-2	101	1.1	1	8.2	0.79	0.19	9.94	8.97	0.14	0.60	0.45
CFP6	30.6	35.0	190	-1	101	2.4	8	8.1	0.79	0.19	12.76	11.78	0.18	0.91	0.73
CFP7	29.6	35.0	192	-2	101	1.0	1	8.2	2.36	0.15	9.46	6.95	0.16	0.55	0.39
<i>August, 2002</i>															
CFP1	29.6	36.0	187	6	97	5.1	10	8.1	1.50	1.28	15.26	12.48	0.17	0.95	0.77
CFP2	29.6	36.3	193	-1	100	5.3	5	8.2	1.21	0.19	13.40	11.99	0.06	0.87	0.81
CFP3	28.6	36.8	196	-2	101	2.0	0	8.2	0.43	0.13	10.36	9.80	0.04	0.64	0.59
CFP4	28.8	36.9	195	-2	101	1.2	0	8.3	0.50	0.10	8.85	8.25	0.02	0.51	0.49
CFP5	29.0	36.7	199	-6	103	1.8	1	8.3	0.71	0.12	9.98	9.15	0.02	0.60	0.58
CFP6	29.8	36.3	205	-14	107	2.7	3	8.2	0.79	0.09	12.65	11.78	0.06	0.71	0.66
CFP7	28.9	36.8	199	-6	103	1.4	0	8.3	0.93	0.14	9.08	8.01	0.03	0.54	0.51

are also characterized by high values of TDP. In the lower Cape Fear River and New River estuaries, concentrations of both total dissolved species are higher or at the same level as maximal concentrations measured at the shelf.

Although maximum concentrations of TDN and TDP do not always coincide with those of DON/DOP, there is

a similarity in distributions of both pools: areas located inshore are also characterized by significantly higher concentrations of DON and DOP. The highest concentrations of ammonium were found in the Cape Fear River Estuary (Table 2). Even in the mixing zone between the Cape Fear River and shelf water, ammonium values were still high (Table 3). In the New River

Table 4

Temperature (°C), salinity, dissolved oxygen, apparent oxygen utilization (AOU; both in $\mu\text{mol kg}^{-1}$), DO saturation (%), Chl *a* ($\mu\text{g l}^{-1}$), turbidity (Turb.; NTU), pH, N and P species (μM) concentrations in Onslow Bay in February and June, 2002 (s=surface, m=mid-depth, b=bottom)

Station	T	S	O ₂	AOU	O ₂	Chl <i>a</i>	pH	NH ₄ ⁺	NO ₃ ⁻	TDN	DON	HPO ₄ ²⁻	TDP	DOP	
<i>February, 2002</i>															
OB27s	14.4	36.6	247	0.1	100	0.16	8.5	0.54	0.07	6.27	5.66	0.11	0.33	0.22	
OB27m	13.9	36.6	243	0.1	100	0.18	8.5	0.45	0.09	5.89	5.35	0.10	0.34	0.24	
OB27b	13.5	36.6	252	0.1	100	0.20	8.5	0.52	0.13	6.49	5.86	0.13	0.36	0.24	
OB63s	20.4	36.4	221	0.1	100	0.41	8.5	0.53	1.87	6.82	4.43	0.19	0.39	0.21	
OB63m	20.0	36.4	223	0.1	100	0.25	8.5	0.60	2.08	7.68	5.00	0.19	0.44	0.25	
OB63b	18.3	36.4	230	0.1	100	0.11	8.4	0.59	8.41	12.64	3.64	0.50	0.68	0.19	
<i>June, 2002</i>															
OB5s	26.4	36.3	200	0	100	0.23	8.3	0.80	0.20	16.72	15.72	0.15	0.43	0.28	
OB5m	26.4	36.3	200	0	100	0.27	8.3	0.79	0.19	8.39	7.41	0.14	0.38	0.24	
OB5b	26.4	36.3	200	0	100	0.30	8.3	0.73	0.17	13.56	12.66	0.15	0.41	0.26	
OB27s	27.0	36.3	198	0	100	0.09	8.3	0.84	0.21	6.85	5.80	0.15	0.32	0.17	
OB27m	26.7	36.3	198	0	100	0.08	8.3	0.82	0.22	5.59	4.55	0.14	0.32	0.18	
OB27b	26.9	36.3	198	0	100	0.05	8.3	0.92	0.22	5.73	4.59	0.11	0.34	0.23	

Estuary, ammonium concentrations were significantly lower than in the Cape Fear River Estuary. In most of the tidal creeks ammonium concentrations were higher than $1\ \mu\text{M}$. The lowest ammonium values were measured in the Cape Fear River plume (Table 3) followed by Onslow Bay (Table 4).

In each area, large ranges of concentrations characterize the distribution of nitrate and *o*-phosphate. Highest values of both mineral N and P species are found upstream in the Cape Fear River (Table 2). In the New River estuary, nitrate concentrations are two orders of magnitude lower than in the Cape Fear River Estuary. Intermediate levels of both nitrate and *o*-phosphate were

measured in tidal creeks, and minimum concentrations in the shelf water.

3.2. N and P species in relation to salinity

In all tributaries, concentrations of N and P species decrease in direction from inshore to the shelf water simultaneously with increasing salinity (Figs. 2 and 3). Two features can be determined in the relationship between nutrients vs. salinity: (i) not every chemical parameter correlates with salinity, and (ii) the same chemical parameter does not correlate with salinity in every area. Figs. 2 and 3 illustrate those parameters

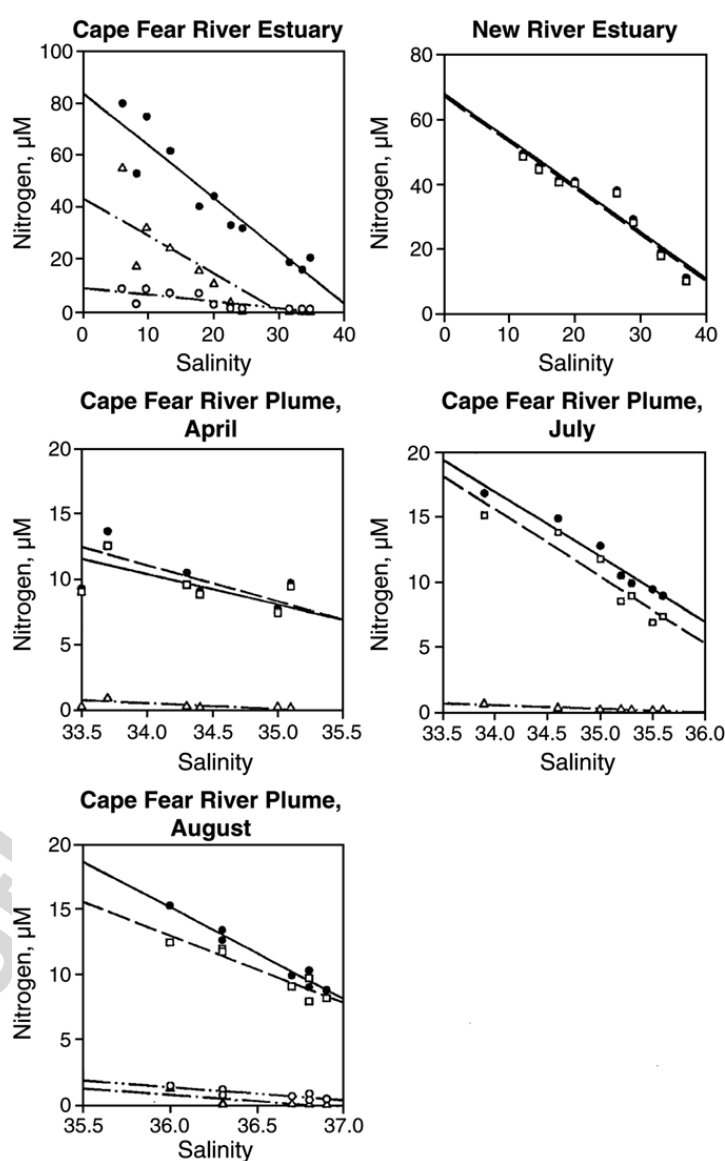


Fig. 2. Nitrogen vs. salinity relationships in coastal and shelf waters of the Cape Fear River, the Cape Fear River plume and the New River estuaries: TDN (closed circles), DON (open square), nitrate (open triangle) and ammonium (open circle). Regression lines as follows: TDN vs. salinity (solid line), DON vs. salinity (short dash line), nitrate vs. salinity (dash-dot line) and ammonium vs. salinity (dash-dot-dot line). Slope and intercept of regressions are presented in Table 5. Note different scales for N species and overlap of symbols in the New River Estuary.

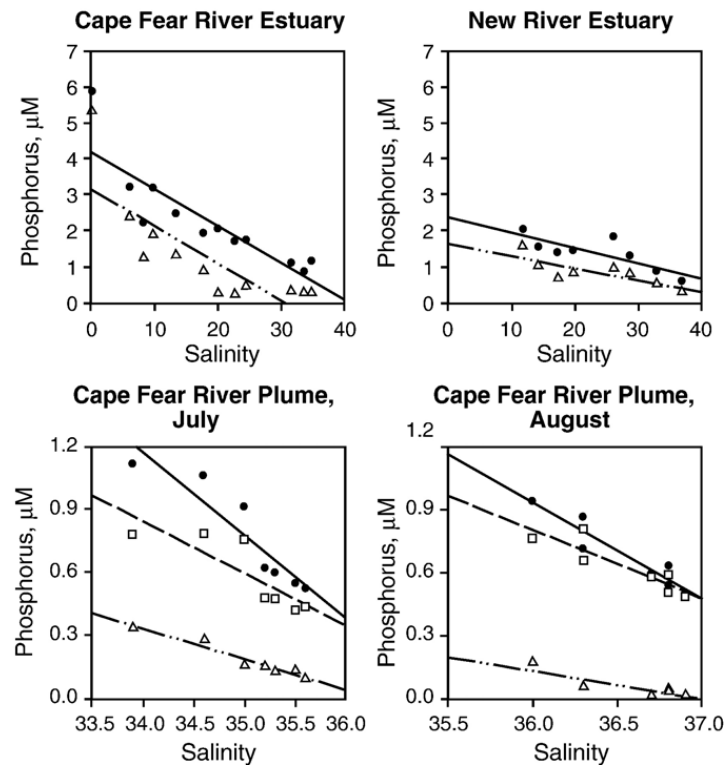


Fig. 3. Phosphorus vs. salinity relationships in coastal and shelf waters of the Cape Fear River and the New River estuaries: TDP (closed circles and solid line), DOP (open square and short dash-dot line) and *o*-phosphate (open triangle and dash-dot-dot line). Slope and intercept of regressions are presented in Table 6. Note different scales for P species.

which were correlated with salinity ($p < 0.05$); slopes and intercepts of these regressions are given in Tables 5 and 6. In the Cape Fear River and New River estuaries, regressions between total dissolved N, P and *o*-phosphate vs. salinity are significant ($p < 0.05$) suggesting a conservative mixing in distribution of these species. In the Cape Fear River Estuary, DON and DOP do not correlate with salinity, indicating that processes different than mixing are involved in the decrease of DON/DOP concentrations with the increase of salinity. However, in the New River

Estuary, DON has a conservative distribution. Nitrate correlates with salinity in tidal creeks, the Cape Fear River Estuary and the Cape Fear River plume in April and July. Ammonium showed conservative mixing only in the Cape Fear River Estuary and Cape Fear River plume in August; in other areas ammonium vs. salinity diagrams consistently demonstrated non-conservative mixing as a result of ammonium consumption or production. DOP and *o*-phosphate yielded conservative mixing only in the Cape Fear River plume in July and August.

Table 5
Relationship of different N species vs. salinity for samples collected in the coastal waters of Onslow and Long Bays

Area	TDN			DON			NO ₃ ⁻			NH ₄ ⁺		
	Slope	Intercept	<i>r</i> ²	Slope	Intercept	<i>r</i> ²	Slope	Intercept	<i>r</i> ²	Slope	Intercept	<i>r</i> ²
Tidal Creeks	-0.4514	39.048	0.1543	0.523	35.022	0.2203	-2.826	33.768	0.6859	0.068	1.239	0.0977
New River	-1.4166	68.120	0.9221	-1.418	67.286	0.9208	0.001	0.070	0.0481	0.001	0.764	0.0032
Cape Fear River	-2.0093	83.985	0.8839	-0.350	31.951	0.2259	-1.425	43.294	0.7173	-0.234	8.741	0.5934
CFR plume, April	-2.6909	102.58	0.7782	-2.251	86.955	0.7800	-0.399	14.093	0.7697	-0.041	1.534	0.0521
CFR plume, July	-4.9415	184.92	0.9561	-5.118	189.560	0.9010	-0.238	8.573	0.8755	0.414	-13.212	0.1714
CFR plume, Aug.	-7.0098	267.53	0.9651	-5.142	198.100	0.8875	-0.921	33.950	0.5160	0.947	35.474	0.7089
Onslow Bay, Febr.	-14.152	524.17	0.3764	6.329	-226.03	0.6935	-20.130	736.850	0.4676	-0.351	13.352	0.4893
Onslow Bay, June	-784.44	28491.0	0.5733	-814.54	295.830	0.5931	5.775	209.470	0.5160	24.328	-882.450	0.3308

Significant coefficients of correlations are marked in bold ($p < 0.05$).

Table 6

Relationship of different P species vs. salinity for samples collected in the coastal waters of Onslow and Long Bays

Area	TDP			DOP			HPO ₄ ²⁻		
	Slope	Intercept	r ²	Slope	Intercept	r ²	Slope	Intercept	r ²
Tidal Creeks	-0.0478	2.3993	0.1806	-0.0362	1.5899	0.2398	-0.0116	0.8094	0.0567
New River	-0.0418	2.4150	0.6504	-0.0089	0.7481	0.1771	-0.0329	1.6669	0.6303
Cape Fear River	-0.1025	4.2013	0.7474	-0.0006	1.0598	0.0004	-0.1019	3.1415	0.6327
CFR plume, April	-0.1591	6.0880	0.5794	-0.1446	5.4692	0.5837	-0.0146	0.6187	0.5091
CFR plume, July	-0.3947	14.5870	0.8588	-0.2471	9.2389	0.7154	-0.1477	5.3476	0.9428
CFR plume, August	-0.4603	17.5100	0.8925	-0.3250	12.5080	0.8018	-0.1353	5.0023	0.7128
Onslow Bay, Febr.	-0.8067	29.8660	0.4435	0.0844	-2.8604	0.1780	-0.8067	29.866	0.4435
Onslow Bay, June	-10.6310	386.340	0.8335	-8.3041	301.730	0.6849	-2.3264	84.6050	0.2341

Significant coefficients of correlations are marked in bold ($p < 0.05$).

3.3. Biogeochemical processes in the coastal and shelf waters

3.3.1. Tidal creeks

As is evident from Table 2, physical, chemical and biological properties not only varied between tidal creeks, but also within each creek, depending upon location. The distributions of chemical species in tidal creeks were affected by: (1) natural processes (*i.e.*, production and remineralization of OM; (2) by anthropogenic input, or (3) by a combination of 1 and 2. Tidal creeks represent the shallowest estuaries, somewhat warmer, with notable inputs of fresh water and terrestrial sediment, and significant amounts of OM buried in bottom sediments (MacPherson et al., *in press*). Tidal flushing of these mini-estuaries occurs during each tidal cycle, affecting water column turbidity. As a result, tidal creeks represented the most turbid environments over the whole study area (Table 2). However, there was a discrepancy between high Chl *a*, high turbidity and DO under-saturation values. We do not preclude that this pigment could indicate the periodic presence of microphytobenthos remobilized by tidal mixing and further advection along the creeks.

In Motts and Bradley Creeks, low DO, DO under-saturation and elevated AOU suggested active mineralization of OM. High Chl *a* concentration in these creeks could be attributed either to *in situ* production or advection of phytopigment from lower parts of creeks or from upstream areas. DO under-saturation indicates potentially high sediment oxygen demand (SOD) or biochemical oxygen demand (BOD). In these tidal creeks BOD is significantly correlated with water column Chl *a*, and SOD concentrations at times can considerably exceed BOD (MacPherson et al., *in press*). Although in all other tidal creeks high phytopigment content was also observed, DO under-saturation in these creeks indicated elevated respiration exceeding production of OM during this period.

In Hewletts and Howe Creeks, DO over-saturation, negative AOU, high dissolved oxygen, Chl *a*, pH, DON, DOP values and low nitrate and moderate *o*-phosphate concentrations indicated phytoplankton production in these locations. Additionally, high ammonium and DON concentrations in these creeks suggest OM input, probably *via* non-point source runoff of pet waste and manures from urban and suburban wildlife, followed by DON mineralization. High *o*-phosphate concentrations in Hewletts Creek indicated the input of DIP from fertilizers, presumably from golf courses located nearby.

Most of the tidal creeks studied were located in a rapidly growing urban area (Wilmington with suburbs). High concentrations of DON in Pages, Barnards, Whiskey, Hewletts, Bradley and Howe Creeks and DOP in Hewletts Creek suggested that the major source of N and P was untreated non-point source runoff of OM and animal waste. The watersheds of these tidal creeks are sewerred and lack septic systems, with the exception of Futch Creek. Higher ammonium concentrations in Futch, Whiskey and Hewletts Creeks indicated that DON was either mineralized to ammonium or ammonium is directly loaded from anthropogenic sources, which in turn are nitrified. The additional potential source of nutrients to Futch Creek could be several freshwater springs located along the south side of the main channel (Mallin et al., 2004).

Nitrate and *o*-phosphate concentrations in Barnards, Motts, Whiskey and Bradley Creeks illustrated that these creeks were affected by the input of fertilizers. The ammonium concentration was higher in Futch Creek possibly due to heavy fertilization occurring at a golf course, which is located within the drainage basin of the study area.

3.3.2. Cape Fear River and New River Estuaries

A summed upstream to downstream view across all stations in the Cape Fear River and New River estuaries

Table 7

Partitioning of TDN and TDP between various reservoirs of N and P pools in the different coastal and shelf environments of Onslow and Long Bays (in %)

Area	Nitrogen			Phosphorus	
	NO ₃ ⁻	NH ₄ ⁺	DON	HPO ₄ ²⁻	DOP
Tidal Creeks	7.2	10.1	82.7	37.5	62.5
New River	0.3	2.8	96.9	61.4	38.6
Cape Fear River	28.3	8.2	63.5	44.2	55.8
CFR Plume, April	4.3	1.2	94.5	19	81
CFR Plume, July	86.1	2.1	11.8	22.4	77.6
CFR Plume, August	2.2	7.5	90.3	7.4	92.6
Onslow Bay, February	20.9	7.4	71.7	43.6	56.4
Onslow Bay, June	2.8	11.5	85.7	38.1	61.9

in Table 2 indicates similar behavior for DO, Chl *a*, turbidity and pH, and different behavior for N and P species. Concentrations of all nutrients were significantly higher in the Cape Fear River than in the New River estuaries. In the Cape Fear River, turbidity increased and pH decreased simultaneously with decrease in salinity, while in the New River Estuary both these parameters had quite homogeneous distributions (6 ± 1.7 NTU and 8 ± 0.04 , respectively).

In the Cape Fear River Estuary, concentrations of all N species decreased from up- to downstream following the salinity increase. In the New River Estuary the salinity ranged from only 18.5 to 19.7 and, as a result, nitrate and ammonium showed homogeneous distributions over the whole estuary (0.09 ± 0.03 μ M and 0.78 ± 0.11 μ M, respectively). In the Cape Fear River, concentrations of nitrate and ammonium were higher by factors of 55 and 46, respectively, while the concentration of DON was only slightly lower than in the New River Estuary. Probably these differences were due to the different sources of N compounds from the watersheds in both rivers. Table 2 shows that N is delivered to the Cape Fear River mostly as nitrate, ammonium, and DON, while to the New River mostly

as DON. This result suggests that sources of N to the Cape Fear River could be from the input of OM from sewage effluent and animal waste runoff, and inorganic fertilizers. The most important source of N to the New River Estuary was organic load (Fig. 2), possibly due to animal waste runoff from upstream swine and poultry farms (Mallin, 2000).

P distribution showed a similar trend for both estuaries. *O*-phosphate concentrations decreased from up- to downstream with significantly higher DIP concentrations in the Cape Fear River Estuary than in the New River Estuary. In both estuaries, the DOP pool demonstrated homogeneous distributions between up- and downstream stations (1.07 ± 0.35 μ M for the Cape Fear River Estuary and 0.54 ± 0.19 μ M for the New River Estuary), but showed maximum concentrations in the middle part of both estuaries (1.77 and 0.86 μ M, respectively). These maxima either coincided with the Chl *a* maximum or with areas of point source sewage effluent discharges close to Wilmington and Jacksonville.

3.3.3. Shelf water

The Cape Fear River plume and Onslow Bay sites are separated by Cape Fear and located in different shallow bays (Long and Onslow Bays) at a distance of about 30 km. The configuration of the coastline leads to significant differences in patterns of circulation and terrestrial loads of sediment and nutrients to these ecosystems. The Cape Fear River plume (Table 3) is an area of mixing between the Cape Fear River and shallow shelf waters with a depth of less than 10m. In contrast, Onslow Bay (Table 4) does not receive any significant riverine input but is affected by the exchange with salt marshes and AICWW *via* narrow and shallow inlets in the west, and the Gulf Stream in the east.

In Onslow Bay, salinity, AOU, DO saturation and pH could be characterized as surface oceanic values (Table 4). During February and June, quasi-constant

Table 8

Averaged molar ratios (\pm S.E.) between DO and total dissolved organic and mineral N and P pools from the coastal and shelf waters

Area	O ₂ :TDN		O ₂ :NO ₃ ⁻		O ₂ :NH ₄ ⁺		O ₂ :DON		O ₂ :TDP		O ₂ :HPO ₄ ²⁻		O ₂ :DOP	
Tidal creeks	7	± 1	702	± 8	124	± 4	9	± 1	159	± 4	513	± 7	257	± 5
New River	9	± 1	3060	± 21	321	± 7	9	± 1	191	± 5	319	± 7	505	± 9
Cape Fear River	6	± 1	198	± 14	85	± 3	8	± 1	110	± 3	393	± 6	209	± 4
CFRP, April	22	± 2	692	± 11	3077	± 23	24	± 2	375	± 8	1951	± 18	468	± 9
CFRP, July	17	± 2	876	± 12	173	± 5	20	± 2	272	± 7	1196	± 14	356	± 8
CFRP, August	18	± 2	1425	± 15	269	± 7	20	± 2	299	± 7	5567	± 31	322	± 7
Onslow Bay, February	33	± 3	1417	± 17	446	± 9	49	± 3	599	± 11	1580	± 18	1061	± 15
Onslow Bay, June	25	± 2	954	± 13	233	± 6	30	± 2	563	± 10	1490	± 16	919	± 12

The Redfield molar ratio is O₂:N=8.6 and O₂:P=138.

distributions of AOU and DO saturation (close to 100%) indicated the gas equilibrium between air and shelf water. In general, chlorophyll *a* concentrations were all less than $0.5 \mu\text{g l}^{-1}$. Increased values of nitrate and *o*-phosphate in February, especially at the bottom and mid-depth, could be related to Gulf Stream intrusions (Mallin et al., 2005a), while in June both these mineral compounds showed almost homogeneous distribution ($0.21 \pm 0.03 \mu\text{M}$ and $0.14 \pm 0.02 \mu\text{M}$, respectively). DON/DOP concentrations decreased from the coast to offshore, also demonstrating concentrations typical for the surface open ocean. In Long Bay there were DON and DOP concentrations 2–3× those of Onslow Bay and Chl *a* concentrations 5–10× higher than Onslow Bay (Figs. 2 and 3). The Cape Fear River brought to the shelf mostly organic, rather than inorganic N and P (Table 3; Figs. 2 and 3).

3.4. TDN and TDP compositions

Analysis of TDN and TDP composition showed that in the coastal and shelf waters, dissolved organic N and P (except in the New River Estuary) were always the major components of total dissolved N and P (Table 7). The amount of DON incorporated into TDN was significantly higher than the amount of DOP incorporated into TDP. Predominance of dissolved organic N and P in the shelf waters could demonstrate either an accumulation of these compounds as result of terrestrial input from the blackwater rivers or from phytoplankton exudation; the latter is probably not the case because for most of the stations DO showed saturations lower than 100%. The contribution of nitrate to TDN increased, while *o*-phosphate to TDP decreased in southward direction: from the New River Estuary, through tidal creeks to the Cape Fear River Estuary due to the different watershed mosaics, different levels of applica-

tion of fertilizers and the leaching of dissolved mineral N and P into aquatic systems.

3.5. O_2 :N:P molar ratios

The molar ratio between dissolved oxygen, nitrate and *o*-phosphate in marine phytoplankton and in deep oceanic waters is almost constant (O_2 :N:P=138:16:1; Redfield et al., 1963). Tables 8 and 9 illustrate several features of these ratios: (1) only at the coastal stations are the DO vs. total dissolved and dissolved organic N and P ratios close to 138; (2) at almost all coastal stations with lower salinity, TDN:TDP and DON:DOP ratios were significantly higher than 16; (3) at almost all shelf stations with higher salinity, TDN:TDP and DON:DOP ratios were close to 16; (4) in almost all areas/in all range of salinity, the DIN:DIP ratio was significantly lower than 16.

In the coastal and shelf waters, there was a large contrast between DO vs. nutrient ratios. Table 8 demonstrates that in the coastal water, O_2 :TDN and O_2 :DON ratios were close to 138, while in the shelf water these ratios showed a deficit of N. O_2 : NO_3^- and O_2 : NH_4^+ ratios show that in both ecosystems nitrate-N was more depleted than ammonium-N, suggesting an input of ammonium from remineralization of organic N. Although in the coastal water O_2 :TDP and O_2 :DOP ratios were more than a factor of two higher than 138, these ratios were even higher in the shelf water. Relationships between DO and *o*-phosphate had quite similar behaviors, with lower values in the coastal water and almost a factor of ten higher in the shelf water. The O_2 :DIP ratio suggested a more pronounced deficit of P than did the DO to DOP ratio.

The TDN:TDP=18.4 (± 2.1) indicate that in the shelf water N and P were almost in balance (with the exception of the Cape Fear River plume in July and August), while in the coastal water P was present in slightly limiting concentrations during the sampling period (Table 9). In all coastal environments, the nitrate to *o*-phosphate ratio illustrates that nitrate-N was present in limiting concentrations relative to *o*-phosphate-P. In contrast, this ratio for the Cape Fear River Estuary was relatively high, suggesting either the excessive input of nitrate relative to *o*-phosphate from the watershed or DIP loss in the estuary.

4. Discussion

4.1. Productivity in the coastal and shelf waters

The morphological differences of the Cape Fear River and the New River estuaries determines the

Table 9
Averaged total, organic and mineral molar ratios between N and P pools (\pm S.E.) from the coastal and shelf waters

Area	TDN:TDP	DON:DOP	$\text{NO}_3^-:\text{HPO}_4^{2-}$	$\text{NH}_4^+:\text{HPO}_4^{2-}$
Tidal creeks	24.7 ± 1.6	33.8 ± 1.8	5.7 ± 0.8	8.0 ± 0.9
New River	23.8 ± 1.4	63.3 ± 3.0	0.1 ± 0.1	1.0 ± 0.3
Cape Fear River	21.3 ± 0.6	55.5 ± 2.0	13.2 ± 1.0	4.7 ± 0.6
CFRP, April	16.6 ± 1.2	19.5 ± 1.8	4.0 ± 0.8	1.1 ± 0.4
CFRP, July	15.9 ± 1.1	17.6 ± 1.7	1.5 ± 0.5	9.1 ± 1.2
CFRP, August	16.6 ± 1.2	16.2 ± 1.6	4.8 ± 0.9	23.0 ± 2.0
Onslow Bay,	18.0 ± 1.4	22.4 ± 2.1	6.7 ± 1.2	3.4 ± 0.8
February				
Onslow Bay,	24.8 ± 1.6	34.9 ± 2.4	1.6 ± 0.5	6.8 ± 1.1
June				

The Redfield molar ratio is O_2 :N=8.6 and O_2 :P=138.

patterns of circulation and affects the biological productivity of these systems. The Cape Fear River Estuary is well flushed by river discharge and tidal currents, while the New River Estuary can be characterized by a relatively stagnant regime (Ensign et al., 2004). Attempts to arrange these estuaries by trophic status are dependent on the criteria used for classification. Commonly scientists use the level of Chl *a* as a measure of eutrophy, and according to this criterion the Cape Fear River Estuary has been classified as moderately eutrophic, while the New River Estuary has been classified as highly eutrophic due to symptoms including phytoplankton blooms, bottom-water hypoxia and anoxia, and fish kills (NOAA, 1996; Bricker et al., 1999; Mallin et al., 2005b). Data presented here show that inorganic nutrient concentrations in the New River Estuary were lower than those in the Cape Fear River, which is fed by a much larger watershed (Mallin et al., 1999, 2005b). Periodically algal blooms occur in the upper regions of the New River Estuary, rapidly depleting the nitrate pool (Mallin et al., 2005b). It is notable that in all offshore and lower estuary situations the dissolved nutrient pool was dominated by organic, rather than inorganic N and P. Sampling regimes limited to inorganic species thus miss a potentially usable source of nutrients for both phytoplankton and bacteria.

Upper reaches of the smaller urban tidal creek estuaries can host dense algal blooms, especially during the summer (Table 2). Mallin et al. (2004) have shown that on occasion Hewletts and Howe Creeks could host blooms exceeding $200 \mu\text{g l}^{-1}$ of Chl *a*, *i.e.*, concentrations typical for highly eutrophic systems.

High-clarity and low-nutrient concentrations of shelf water in Long and Onslow Bays predominated during our study (Tables 2 and 3). When intrusions to this shelf of nutrient-enriched slope water occur, they can stimulate blooms and sometimes create a near-bottom Chl *a* maximum (Mallin et al., 2000). During February and June the Onslow Bay shelf water was oligotrophic in terms of phytoplankton abundance, but evidence for bottom and mid-depth nitrate (and to a much lower extent *o*-phosphate) pulses were seen due to Gulf Stream intrusions. Chl *a* concentrations were typically *ca.* $1\text{--}3 \mu\text{g l}^{-1}$ in the Cape Fear River plume in Long Bay, with concentrations of $0.01\text{--}0.20 \mu\text{g l}^{-1}$ in Onslow Bay, with particularly low values close to the Gulf Stream.

4.2. N vs. P limitation

Summer $\text{O}_2\text{:N:P}$ ratios in the coastal and shelf waters of the eastern North Carolina showed that total, inorganic

and organic N and P pools demonstrated different results: the N and P could be present either in limiting or excessive concentrations relative to 138:16:1 ratio depending upon the pool. These discrepancies could be attributed to the combination of different processes: diversity of N and P sources, seasonality, biological availability and chemical behavior.

In the Cape Fear River Estuary, significant P limitation occurs during spring as a result of high winter-spring flow associated with high flux of DIN to the lower estuary, and the remineralization of DON (Mallin et al., 1999). In the upper Cape Fear River Estuary, phytoplankton production is light-limited, whereas in the lower estuary it is N limited during summer and P during spring (Mallin et al., 1999). In the Cape Fear River plume, the DON:DOP ratio decreased from April to August indicating an increase in N-limitation. TDN:TDP and DON:DOP ratios in the New River Estuary indicate potential P limitation, while DIN/DIP ratios suggest N limitation (Table 8). Nutrient addition bioassay experiments in the New River Estuary using inorganic N and P treatments found frequent N limitation of phytoplankton (Mallin et al., 2005b). Our observations suggest that only in the Cape Fear River Estuary was the nitrate to *o*-phosphate ratio close to the Redfield ratio, indicating equivalent inputs of both nutrients from the watershed; in all other areas, there was a severe deficit of DIN relative to DIP. In contrast, in almost all areas the DON:DOP ratio showed a P deficit relative to N (Table 8).

4.3. N and P retention in the Cape Fear River and New River estuaries

Concentrations of almost all N and P species decreased drastically from the upper to lower parts of each estuary, indicating that seaward N and P fluxes are modified by within-estuary transformation of reactive species, the burial of N and P in sediments, and the loss of gaseous N species by bacterial reduction. It is well known that estuaries can serve as large filters or traps (Biggs and Howell, 1984) for material that can be transformed by resident processes (Dame et al., 2000).

To estimate the retention of N and P within each estuary we used TDN and TDP values from the upper and lower stations and available water flow data from different sources. Concentrations of TDN and TDP were multiplied by average annual river discharge or freshwater flow to obtain an estimate of the loads of N and P to the upper and lower part of each estuary. The annual mean water flow value for the Cape Fear River Estuary was taken from Dame et al. (2000). The water flow value for the New River Estuary (the point near Gum Branch, NC) was

obtained from <http://waterdata.usgs.gov>, which presents the annual mean water flow for the period 1950–2001. These loads reflect the amount of N and P entering and exiting each estuary. The difference between two fluxes provides information on the loss of N and P. It should be noted that between upper and lower estuary there were additional N and P sources such as point-source discharges, and smaller creeks draining areas of significant human usage, which are difficult to take into consideration in such an approximation.

During June 2002 (a low flow period) about 41% of N and 48% of P were retained in the Cape Fear River Estuary, while in the New River Estuary these values were lower, 26% and 39%, respectively. A higher level of TDP retention relative to TDN could partly explain the higher degree of P limitation at low salinity/high nutrients than at high salinity/low nutrients. The June N removal in the Cape Fear River was close to that of the 35% presented for the Chesapeake Bay, but it was almost a factor of two lower for P (Boynnton et al., 1995). However, a study utilizing five years of data (Ensign et al., 2004) have shown a much more rapid flushing time for the Cape Fear Estuary (8 days), with subsequent N retention of only 5 to 9% as opposed to the New River Estuary (34–51% N retention).

The differing capacity to retain N and P between the Cape Fear and New River estuaries could be either due to: (i) different rates of N and P consumption by phytoplankton or remineralization by bacteria; (ii) different rates of N-denitrification in bottom sediment; (iii) different quality of sediment capable of retaining both species. In estuaries, denitrification is the most important N removal mechanism (Koike and Sorensen, 1988; Nixon et al., 1996; Mackenzie et al., 2002), while P absorption on sediment surfaces plays the major role in the sink of P (Froelich, 1988; Burkholder, 1992).

The sediments enriched in P that are not deposited in the coastal water are eventually transported to the shelf where P can be desorbed due to a sharp rise in pH (Eyre and Twigg, 1997), or deposited, or redistributed along the shelf. A high-grade phosphorite ore deposit is present in the surface sedimentary layers of Onslow Bay in quantities on the order of 10^9 t (Mallin et al., 2000). In the New River Estuary, which is separated from the shelf by barrier islands, sediment accumulates in the salt marshes along the estuary and finally along the AICWW. Deposition of rich sediment supplies a substrate for dissolved organic N and P reduction and, as a result, an increase in concentrations in the pore water, and a flux to the near-bottom water layer. For example, analysis of the pore water collected in AICWW close to the mouth of Hewletts Creek showed

that the concentration of TDP and TDN varied from 1 to 110 μ M and from 100 to 400 μ M, respectively (T. Molesky, personal communication, 2003).

5. Conclusions

We studied the summer partitioning of N and P species in different coastal and shelf environments of the southeastern NC, and demonstrated the high level of accumulation of most of N and P individual compounds in the oligohaline parts of each tributary. Accumulation of N and P species was attributed to loading from agricultural and urban sources to the coastal watersheds, transported to receiving estuaries. Euhaline parts of estuaries and the shelf are characterized by oceanic surface values, indicating the loss of N and P between oligo- and mesohaline parts of estuaries. We estimated that during June 2002 the loss of N and P from the water column to the sediment was about 41% and 48%, respectively for the Cape Fear River Estuary with a rapid flushing regime, and 26% and 39%, respectively for the New River with a restrained flushing regime. Compared to the five-year mean observation (Ensign et al., 2004), the June estimate for N retention is much higher for the Cape Fear River Estuary (likely due to the low June flow conditions) but similar to that of the New River Estuary.

The $O_2:N:P$ molar ratio demonstrated a spatial gradient from upstream to downstream in availability of N and P for phytoplankton and bacteria. P incorporated in DOP and N incorporated in DIN almost always were limiting nutrients in coastal and shelf waters. This study demonstrated that, with the exception of estuarine headwaters, the dissolved N and P pools were dominated by organic rather than inorganic species.

Finally, despite a high level of anthropogenic impact on the uppermost coastal waters of the southeastern NC, there is self-regulation in this coastal ecosystem with respect to human perturbations which retains significant amounts of the N and P load within the estuaries before it reaches the shelf water.

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