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Agents of change and temporal nutrient dynamics in the Altamaha River Watershed

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Abstract. Nutrient and carbon dynamics in river ecosystems are shifting, and climate change is likely a driving factor; however, some previous studies indicate anthropogenic modification of natural resources may supersede the effects of climate. To understand temporal changes in river ecosystems, consideration of how these agents act independently and collectively to affect watershed biogeochemistry is necessary. Through the Georgia Coastal Ecosystems Long-Term Ecological Research Project, we assessed nutrient (phosphorus, nitrogen, silicate) and carbon dynamics, with specific regard to import and export, in the Altamaha River Basin from 2000 to 2012. This is the first study in the region to document the biogeochemical patterns in the Altamaha's four main tributaries, the Little Ocmulgee, Ocmulgee, Oconee, and Ohoopee rivers, and the relationships between biogeochemistry and historical precipitation and discharge patterns as well as agricultural and population census data. As discharge patterns are a primary driver of nutrient loads, we determined that water use was a dominant factor in the shifting ecosystem dynamics. Dissolved inorganic nitrogen loads were primarily driven by population density and dissolved inorganic phosphorus loads were strongly influenced by livestock biomass. Taken together, we conclude that both the transportation and biogeochemical cycling of nutrients within the Altamaha River Watershed were highly impacted by anthropogenic influences, which were then further exacerbated by continued climate change. Furthermore, the N- and P-loads in the Altamaha River and tributaries were dominated by dissolved organic nitrogen and dissolved organic phosphorus, emphasizing a need to further study the bioavailability of these species and the mechanisms driving their potential ecological impacts.

Key words: biogeochemical; carbon; climate change; nutrients; water quality; watersheds.

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Introduction

The interplay between climate- and human-related impacts on water resources has historically been a challenge to quantify. As populations continue to grow and projected climate change scenarios include more frequent and extreme hydrologic events (Collins et al. 2013), it is increasingly important to understand the factors driving the quality and quantity of water resources. In the United States, maintaining the quality of water supplies, for example, ensuring that the water is potable, was federally mandated by the Clean Water Act of 1972. Since then, programs such as the National Stream Quality Accounting Network (NASQAN) and the U.S. Geological Survey National Water Quality Surveillance System (NWSS) have monitored water quality trends. Despite efforts to maintain both water quantity (e.g., sufficient baseline flows) and quality (e.g., potable supplies), increasing populations and shifting climate regimes call for a more integrated, whole-watershed approach to assess the agents driving change in water resource dynamics (Vörösmarty et al. 2000, Whitehead et al. 2009).

In Georgia, reports on water quantity trends are often in the context of water resource availability in the face of climate-related impacts (Barczak and Carroll 2007, Fanning and Trent 2009, Zhang and Georgakakos 2011, Campana et al. 2012). Water quality assessments are often based on nutrient loads and exports and are viewed in the context of population and land use change (Schaefer and Alber 2007, Weston et al. 2009). While assessments of water quantity and quality are useful separately, these elements cumulatively drive overarching changes in watershed ecological dynamics. For example, drawdown of groundwater resources along the coast, exacerbated by climate-driven sea-level rise (SLR), generates saltwater intrusion into local groundwater (aquifer salinization) and into watershed surface waters (Whitehead et al. 2009, Rotzoll and Fletcher 2013). This decreases the availability of potable groundwater and stimulates the mineralization of organic carbon currently stored in freshwater marshes (Weston et al. 2006, Rotzoll and Fletcher 2013).

Upper-watershed stream water chemistry is also susceptible to alterations resulting from changes in precipitation and discharge regimes. Under warmer temperature conditions, soil nitrate concentrations are expected to accumulate due to increased soil mineralization (Whitehead et al. 2009). Han et al. (2009) and Tian et al. (2015) indicated that total nitrogen (TN) and carbon export from a variety of watersheds is driven temporally by discharge and spatially by land use. Areas experiencing drought and nitrate accumulation, compounded by increased fertilizer inputs, are predicted to be "flushed out" by sudden storm events. This suggests that rivers are susceptible to pulses of nutrient enrichment due to runoff and leaching during such hydrologic events (Whitehead et al. 2009, Lutz et al. 2012, Tian et al. 2015). The consequences of these nutrient pulses can include eutrophication and downstream ecological impacts from nutrients transported to the river mouth.

Here, we use an integrated approach to assess the agents driving patterns of nutrient and carbon dynamics in the Altamaha River Watershed. We use historical precipitation records to assess shifts in local climate patterns and historical discharge records to assess changes in flow of the Altamaha River and its major tributaries in light of anthropogenic impacts. We analyze a 12-year data set (2000–2012), collected through the Georgia Coastal Ecosystems Long-Term Ecological Research Project's water quality monitoring program, to assess nutrient inputs to and exports from the Altamaha River Basin. We consider climate and major anthropogenic factors (i.e., agricultural land use, livestock populations, population density, and river impoundments such as dams) as agents of ecosystem change.

The aim of this work was to provide a baseline for understanding the biogeochemical dynamics, specifically with regard to drivers of imports and exports, in the Altamaha River Watershed. We postulated that anthropogenic impacts will be reflected in increased ammonium loads as a result of increased agricultural land use and livestock density. Population increases will further decrease overall flow in the Altamaha River Watershed. This decrease will be exacerbated by seasonal-reduced flows due to altered precipitation periods and prolonged periods of drought. At these times, nutrient concentrations will increase and anthropogenic sources will be more pronounced. We further hypothesized an increase in nutrient export during heavy rains that followed prolonged dry periods—especially with regard to inorganic nitrogen and phosphorus (Weston et al. 2009, Palomo et al. 2013).

Materials and Methods

Study site

Of the nine major river basins in Georgia, the Altamaha Watershed is the largest. It encompasses the Altamaha (ALT), Ocmulgee (OCM), Little Ocmulgee (LOCM), Oconee (OCO), and Ohoopee (OHO) subwatersheds and drains nearly 35,500 km^2 (Fig. 1; Weston et al. 2009). It transports water from several large metropolitan areas in the upper watershed, including Atlanta, Macon, and Athens, down to the coastal flood plain where it drains into Altamaha Sound and out to the Atlantic Ocean (Fig. 1; Georgia Environmental Protection Division—Georgia EPD 1998, 2004*a*, *b*). The main physiographic provinces underlying the watershed are the Northern Piedmont Province and the Coastal Plain Province (Georgia EPD 1998). The northern

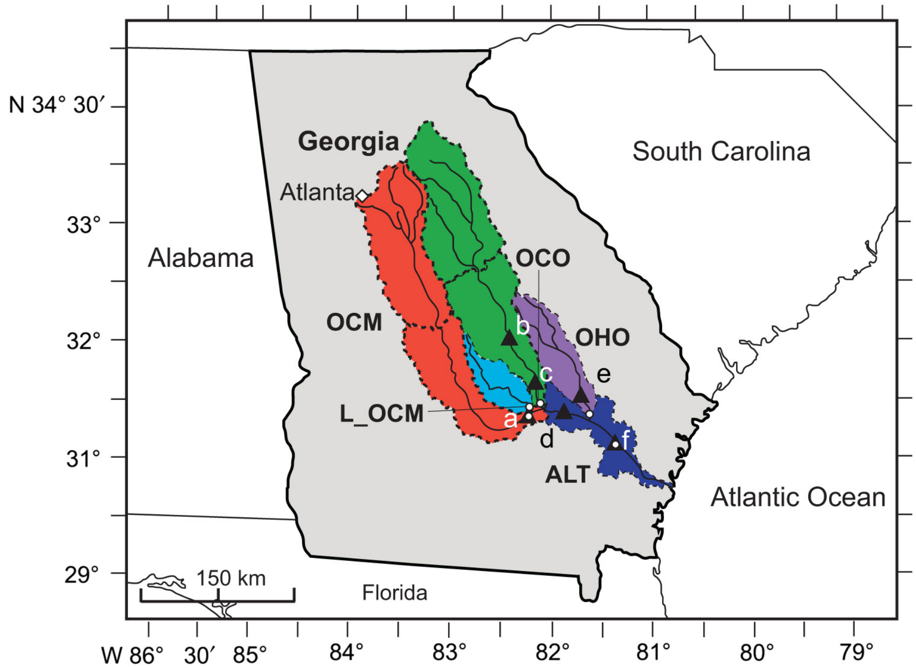

Fig. 1. Map of the Altamaha River Watershed. Dashed lines and colors outline the Altamaha River subwatersheds. White dots indicate sampling locations on the Ocmulgee (OCM), Little Ocmulgee (LOCM), Oconee (OCO), and Ohoopee (OHO) rivers just before their confluence with the Altamaha (ALT) River. Triangles indicate U.S. Geological Survey (USGS) stations from which current and historical discharge data were accessed (2000–2012): (a) Lumber City (USGS 02215500), (b) Dublin (USGS 02223500), (c) Mt. Vernon (USGS 02224500), (d) Baxley (USGS 02225000), (e) Reidsville (USGS 02225500), and (f) Doctortown (USGS 02226000). Shaded regions outlined with dotted lines indicate watershed boundaries.

halves of the Ocmulgee and Oconee subwatersheds lie in the Northern Piedmont Province, which is characterized by crystalline and metamorphic igneous rocks and steep elevation gradients (Georgia EPD 1998, 2004*b*). While the overlying clays in the Piedmont Province generally protect the underlying aquifer from pollution, water yields are unpredictable. Thus, the local municipalities in this area rely mostly on surface water resources in the upper parts of the Oconee and Ocmulgee subwatersheds (Georgia EPD 1998, 2004*b*, Fanning and Trent 2009).

In contrast, the lower subwatersheds lie in the Coastal Plain Province, which is comprised mainly of shallow marine sediments including sand and kaolin (Georgia EPD 1998). The underlying Floridan Aquifer is one of the most productive aquifers in the United States (Georgia EPD 1998). As a result, the southern half of the Altamaha River Watershed is more reliant on groundwater resources (Georgia EPD 2004*a*, Fanning and Trent 2009). From the northwest to the southeast, the Altamaha River Watershed decreases in slope gradient, clay content, and depth to the water table. With the transition to the Coastal Plain Province, flood plains become more prominent. This drives soils from moderately well drained to poorly drained despite a shift from clays to sand (Georgia EPD 1998, 2004*a*, *b*).

Sample collection and data analysis

Altamaha River water samples were collected from September 2000 through December 2012. From 2005 to 2012, samples were collected approximately weekly. From 2002 to 2004, samples were collected either monthly or bimonthly. Samples from the Little Ocmulgee (LOCM) were collected either monthly or seasonally from September 2002 to April 2005. In the Ocmulgee (OCM), Oconee (OCO), and Ohoopee (OHO) tributaries, sample collections were primarily event-driven; monthly samples were collected between October 2000 and March 2012. In total, 528 samples were collected from the Altamaha River (ALT) at Doctortown, Georgia, and 254 samples were collected from the LOCM, OCM, OCO, and OHO tributaries.

Instantaneous discharge data were accessed from the U.S. Geological Survey (USGS) website. The stations referenced for discharge and precipitation data included Baxley (USGS 02225000, Altamaha), Doctortown (USGS 02226000, Altamaha), Lumber City (USGS 02215500, Ocmulgee), Mt. Vernon (USGS 02224500, Oconee), Dublin (USGS 02223500, Oconee), and Reidsville (USGS 02225500, Ohoopee; Fig. 1). For instances where historical data were unavailable, discharge values were estimated from the monthly average percent contribution of each tributary to the discharge at either the Baxley or Doctortown USGS stations between 2010 and 2013.

Historical precipitation data between 1895 and 2012 were referenced from the Southeast Regional Climate Center (SERCC) website (www.sercc.com, accessed between December 2012 and January 2014). State average monthly and annual precipitation statistics were calculated to determine "flood" and "drought" years and months during the study period (Appendix S1: Table S1). "Drought" months were defined as those with recorded precipitation totals lower than one standard deviation below the mean. "Flood" months were those that recorded precipitation totals greater than one standard deviation above the mean.

Agricultural land use and livestock numbers were acquired from the U.S. Department of Agriculture, 1969 and 2007 Georgia State Census of Agriculture. Population numbers were from the U.S. Department of Commerce, 1969, 2000, and 2010 Censuses of Population and Housing. The proportion of agricultural land use, livestock, and population densities in each watershed sub-basin were calculated from the county proportions noted by Weston et al. (2009).

The concentrations of dissolved inorganic phosphate (DIP, measured as PO_4^{3-}), total dissolved phosphorus (TDP), dissolved organic phosphorus (DOP), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), dissolved inorganic nitrogen (DIN), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), silicate (Si), and total suspended solids (TSS; 2006–2012) were analyzed using standard methods outlined in Table 1. Upon collection, samples were filtered through ashed GF/F filters and stored in HDPE bottles until analysis. All analyses were conducted within 6 months of sample collection.

Calculations and statistical methods

We compared the relationship between nutrient parameters and instantaneous discharge using log–log regressions (Godsey et al. 2009, Gallo et al. 2015). The coefficients of determination (R^2) identified how much variation in geochemical concentration could be explained by discharge in each watershed sub-basin. The slopes (β_1) of each regression indicated whether or not each catchment was chemostatic (indicated when $\beta_1 = 0$). If the catchment is chemostatic, geochemical concentrations and hydrology are independent of each other implying that within-system processing drives the static conditions. This indicates that the net amount of a geochemical parameter transported through the watershed is largely dependent on the hydrologic conditions. In other words, if nitrate behaves chemostatically, then the export of nitrate out of the watershed will be strongly correlated with discharge. A significant negative slope ($P < 0.05$) indicated dilution of a geochemical parameter with an increase in water yield, whereas a significant positive slope ($P < 0.05$) indicated addition of a given parameter (likely due to increased external inputs such as runoff, precipitation, or erosion) with an increase in water yield.

To further elucidate the dynamics of each catchment, instances in which a geochemical parameter did not fall within the constraints of the 95% confidence interval of the log–log regression models were further assessed. For these instances, trends (if any) in geochemical concentrations as a result of flood condition and/or season were observed. In Georgia, the seasons are classified as follows: fall—September through November; winter—December through February; spring—March through May; and summer—June through July. We classified hydrologic conditions based on the median, 25th (P25), and 75th (P75) percentiles calculated from the discharge

Table 1. A summary of the analytical methods used to measure and/or calculate each parameter.

Parameter measured	Analytical method
Phosphate (PO_4^{3-})	Standard analyzer protocol (Lachat Instruments FIA 8000 Autoanalyzer Method 31-115-01-1-H)
Total dissolved phosphorus (TDP)	High-temperature combustion and hydrolysis (Shimadzu Instruments Spectrophotometer Model: UV-1601; Monaghan and Ruttenberg 1999)
Dissolved organic phosphorus (DOP)	Calculated as the difference between TDP and PO_4^{3-}
Ammonium (NH_4^+)	Standard colorimetric phenolhypochlorite method (Shimadzu Instruments Spectrophotometer Model: UV-1601; Solorzano 1969)
Nitrite (NO_2^-)	Standard analyzer protocol (Lachat Instruments FIA 8000 Autoanalyzer Method 31-107-04-1-A)
NO_x: Nitrate + Nitrite (NO_3^- + NO_2^-)	Standard analyzer protocol (Lachat Instruments FIA 8000 Autoanalyzer Method 31-107-04-1-A)
Nitrate (NO_3^-)	Calculated as the difference between NO_x and NO_2^-
Total dissolved nitrogen (TDN)	Oxidative combustion–chemiluminescence (Shimadzu Instruments TOC 5000 coupled to an Antek Instruments model 7020 NO analyzer; Álvarez-Salgado and Miller 1998) and (Shimadzu Instruments TOC-Vcsn coupled to Shimadzu Instruments TN unit)
Dissolved organic nitrogen (DON)	Calculated as the difference between TDN and DIN (NO_x + NH_4^+)
Dissolved organic carbon (DOC)	Oxidative combustion–infrared analysis (Shimadzu Instruments TOC 5000 and Shimadzu Instruments TOC-Vcsn)
Dissolved inorganic carbon (DIC)	Measured through an automated DIC analyzer with a nondispersive infrared CO_2 analyzer (Li-Cor 6252; see Wang and Cai 2004)
Silicate (SiO_2)	Standard analyzer protocol (Lachat Instruments FIA 8000 Autoanalyzer Method 31-114-27-1-A)
Total suspended solids (TSS)	Sample filtered through GF/F filters (0.7 μm), dried, and weighed to the nearest 0.001 mg

(Q) records of each sub-basin: "Dry"—Q < P25; "Median"—Q = P25–P75; and "Flood"—Q > P75. We integrated these data with our results to determine whether any relationships between geochemical parameter, discharge, and precipitation were apparent.

Export values ($kmol \cdot km^{-2} \cdot yr^{-1}$) of each parameter were estimated by multiplying the discrete concentration (μM) observations by instantaneous discharge (Q, m^3/s) and then dividing by total area of each subwatershed (km^2).

Spearman's rho nonparametric correlation coefficients were calculated to identify relationships between parameter export and population density, livestock density, and proportion of agricultural land area used for agriculture in each subwatershed, respectively. The nonparametric Kruskal–Wallis and post hoc Mann–Whitney *U* tests were used to analyze differences between monthly historical state precipitation patterns and differences in nutrient or carbon concentrations between the tributaries and Altamaha River. Stepwise and backward multiple linear regressions were performed on the average daily flow of each river to determine which tributary best predicted Altamaha River flow.

All statistical analyses were conducted using PASW Statistics Student Version 18 and R (http://www.r-project.org/).

Results

Nitrogen

The results of the simple log–log regressions comparing each nitrogen parameter with discharge are presented in Table 2. No relationship between discharge and TDN was demonstrated in the Altamaha, Oconee, or Ohoopee River. The Little Ocmulgee showed a significant positive relationship with discharge ($R^2 = 0.258$, $P < 0.01$), while the Ocmulgee demonstrated a slight, but significant, negative relationship ($R^2 = 0.054$, $P < 0.05$). An analysis of the data points lying outside the 95% confidence interval of the log–log regression showed that across the Altamaha Watershed, the instances in which TDN concentrations were lower than expected generally occurred during the summer or early fall (June, July, August, or September). These were often the same sampling days in which log-DIN (NO_3^- + NO_2^- + NH_4^+) concentrations were also low (Fig. 2).

Table 2. A summary of the simple log–log linear regressions describing the variance of each nitrogen parameters (concentration, μM, or ratio): nitrate (NO_3^-), nitrite (NO_2^-), NO_3^- + NO_2^- (NO_x), ammonium (NH_4^+), dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), and the dissolved organic nitrogen: dissolved inorganic nitrogen ratio (DON:DIN) as described by discharge.

Regression summary, by site	NO_3^-	NO_2^-	NO_x	NH_4^+	DIN	DON	TDN	DON:DIN
Altamaha								
β_1	−0.029	−0.006	−0.021	0.092	−0.067	0.192	0.018	0.260
R^2	0.001	0.000	0.000	0.015	0.007	0.121	0.004	0.052
P-value	0.571	0.885	0.660	**0.006**	0.062	**<0.001**	0.167	**<0.001**
df	518	521	522	521	513	501	524	517
Oconee								
β_1	0.079	−0.013	0.059	0.172	0.042	0.076	0.042	0.032
R^2	0.006	0.000	0.004	0.056	0.003	0.072	0.030	0.002
P-value	0.529	0.879	0.588	**0.042**	0.616	**0.019**	0.136	0.733
df	74	73	73	74	71	71	73	73
Ocmulgee								
β_1	−0.420	0.045	−0.278	0.146	−0.255	0.195	−0.065	0.455
R^2	0.395	0.002	0.087	0.035	0.149	0.088	0.054	0.175
P-value	**<0.001**	0.693	**0.010**	0.113	**0.001**	**0.011**	**0.045**	**<0.001**
df	71	72	71	73	71	71	74	71
Little Ocmulgee								
β_1	0.083	−0.025	0.065	0.174	0.104	0.097	0.113	−0.007
R^2	0.027	0.002	0.018	0.187	0.088	0.189	0.258	0.000
P-value	0.447	0.837	0.503	**0.024**	0.141	**0.027**	**0.006**	0.920
df	24	24	25	26	22	23	25	24
Ohoopee								
β_1	−0.429	−0.027	−0.372	−0.139	−0.323	0.146	0.034	0.468
R^2	0.359	0.004	0.409	0.094	0.403	0.262	0.039	0.483
P-value	**<0.001**	0.603	**<0.001**	**0.008**	**<0.001**	**<0.001**	0.093	**<0.001**
df	72	71	72	72	70	70	72	71

Note: The *P*-values in bold indicate the slope of the relationship is significantly different from zero ($P < 0.05$).

The median DIN concentrations in the Altamaha (23.5 μM) and Ocmulgee (30.6 μM) rivers exceeded the world averages reported by Meybeck (1982), who reported a range of 50–250 μg L^{-1} or 4–18 μM in natural surface waters (Appendix S1: Table S2). Log-DIN, NO_x, and NO_3^- concentration vs. log-flow reflected similar patterns across the watershed. The log–log regression slopes of the Oconee, Little Ocmulgee, and Altamaha rivers were not significantly different from zero, whereas in the Ocmulgee and Ohoopee rivers, the slopes were significantly negative (Table 2; $P < 0.01$). Discharge described between 9 and 41% of the variability in these parameters. There was no demonstrable log–log relationship between NO_2^- and discharge in any of the tributaries, while NH_4^+ demonstrated slight, but significant, positive relationships with discharge in the Altamaha, Oconee, and Little Ocmulgee rivers ($P < 0.05$). There was a significant negative relationship in the Ohoopee Tributary ($P < 0.01$).

In the Oconee, Ohoopee, and Little Ocmulgee tributaries, the dominant N-form was DON. In the Ocmulgee Tributary and Altamaha River, the dominant N-form is DIN (Appendix S1: Table S2). There was a significant, positive log–log relationship between DON and discharge across all tributaries and the Altamaha River (Table 2; $P < 0.05$). In contrast to the DIN observations, further analysis of the log–log regressions comparing DON concentrations with discharge indicated that the majority of instances in which DON concentrations were lower than expected did not occur during the summer months (Fig. 3). Furthermore, higher-than-expected DON:DIN ratios tended to be a result of decreased DIN concentrations, whereas lower-than-expected ratios tended to be a result of decreased DON concentrations. There were no cases in which the DON:DIN ratio was

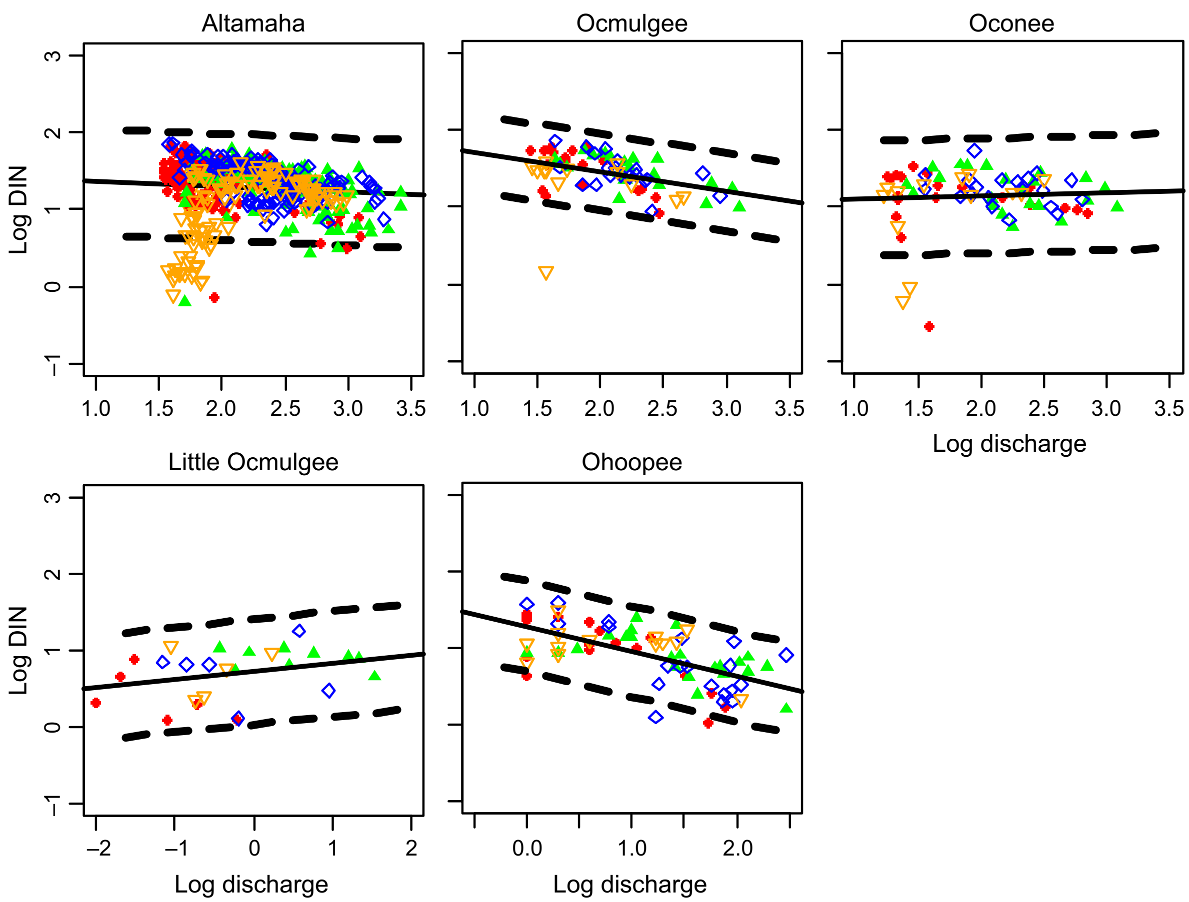

Fig. 2. Log–log regressions comparing the relationship between dissolved inorganic nitrogen (DIN) concentration and discharge in the Altamaha, Ocmulgee, Oconee, Little Ocmulgee, and Ohoopee rivers. Color and symbols indicate different seasons. Red circles represent fall, blue diamonds represent winter, green triangles represent spring, and orange triangles represent summer. The solid line is the plotted log–log linear regression, and the dashed lines indicate 95% confidence interval.

higher or lower than expected as a result of conspicuously high DON or DIN concentrations.

N-export calculations indicated a strong relationship between DIN (specifically NO_3^-) and population density (Fig. 4a, b; Spearman's rho, $n = 4$, df = 2, $P < 0.01$). The Ocmulgee River subwatershed, which supported the largest population density, had the highest overall TDN concentration and export (Table 3, Fig. 5; Kruskal–Wallis, $\chi^2 = 80.01$, df = 4, $P < 0.001$). This was reflected in the high DIN export, specifically in terms of nitrate (Fig. 5; Kruskal–Wallis, $\chi^2 = 145.52, 167.75$, df = 4, $P < 0.001$). The export of ammonium was similar in the Oconee and Ocmulgee River subwatersheds (Fig. 5) and demonstrated a positive, although not significant, relationship with livestock biomass (Fig. 6a). Interestingly, NO_3^- and DIN export exhibited a significant negative relationship with the proportion of agricultural land across the watershed (Fig. 6b, c; Spearman's rho, $n = 4$, $P < 0.01$). TDN export had a similar relationship, but was not significant (Fig. 6d). The overall shallow slopes observed in the log–log relationships between nutrient concentrations and discharge ($-0.5 < \beta_1 < 0.5$) indicated that the nitrogen export out of the Altamaha River Watershed was driven largely by water yield.

Phosphorus

The simple linear log–log regressions between all phosphorus parameters and discharge are presented in Table 4. TDP and discharge across all

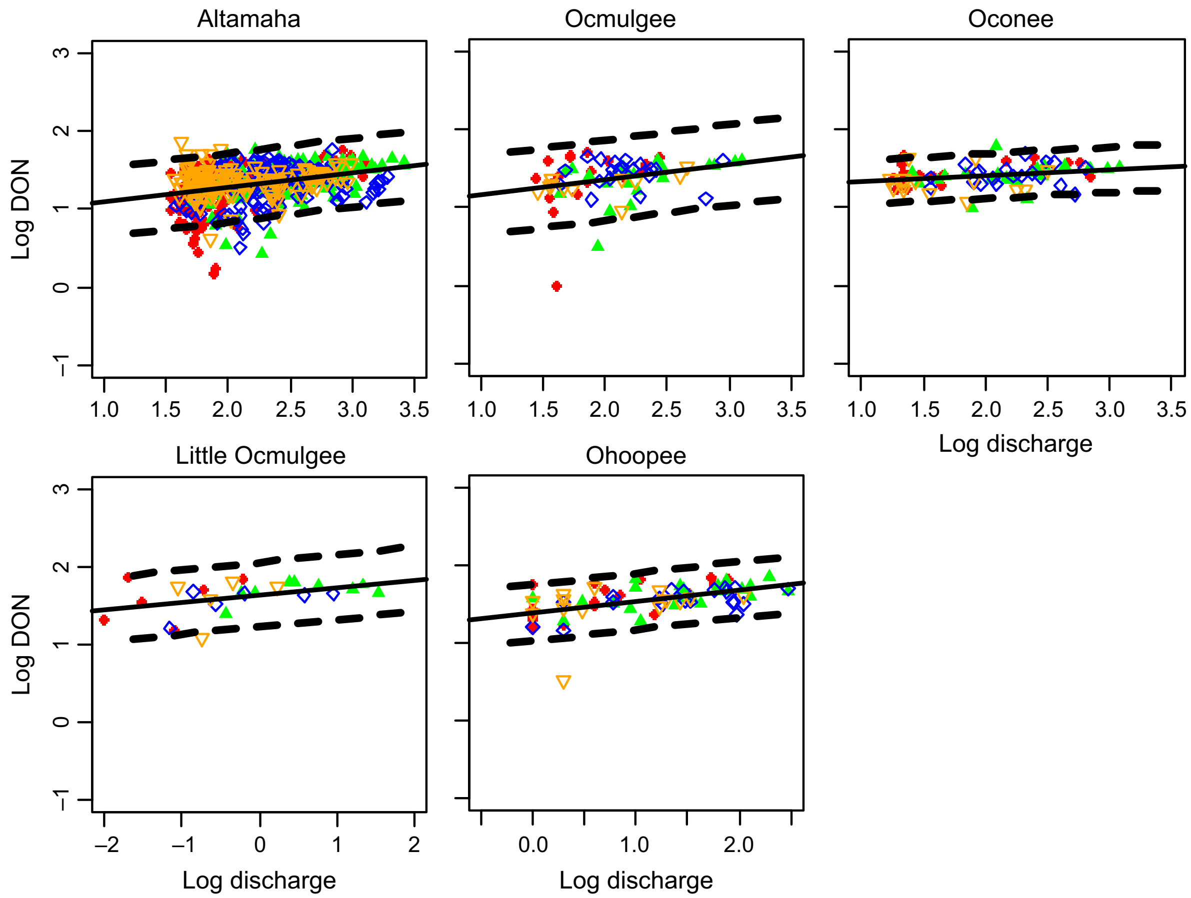

Fig. 3. Log–log regressions comparing the relationship between dissolved organic nitrogen (DON) concentration and discharge in the Altamaha, Ocmulgee, Oconee, Little Ocmulgee, and Ohoopee rivers. Color and symbols indicate different seasons. Red circles represent fall, blue diamonds represent winter, green triangles represent spring, and orange triangles represent summer. The solid line is the plotted log–log linear regression, and the dashed lines indicate 95% confidence interval.

tributaries and the Altamaha River demonstrated slopes that were not different from zero. Significant negative relationships were observed between discharge and DIP in the Altamaha River and Ohoopee Tributary ($P < 0.001$). The Ohoopee showed the strongest relationship, with discharge describing 22% of the variability in DIP concentration. Slight but significantly positive relationships between DOP and DOP:DIP ratio and discharge respectively ($P < 0.05$) were observed in the Oconee, Ocmulgee, Ohoopee, and Altamaha rivers. With the exception of the DOP:DIP ratio in the Altamaha River, discharge explained less than 10% of the variability of either parameter ($P < 0.05$).

The days on which the DIP concentrations fell outside the 95% confidence interval of the log–log linear regression model or were lower than predicted by the model occurred during the summer or fall months (June through November) across the Altamaha River and tributaries. One exception occurred in May 2005 in the Altamaha River (Fig. 7). Conversely, the sampling days in which DOP concentrations were lower than expected rarely occurred in the summer. Instances that were higher than expected occurred in fall and winter (Fig. 8; October through January).

The median DIP concentration was the highest in the Oconee Tributary (0.79 μM), and the lowest in the Little Ocmulgee (0.26 μM). These medians are in relative agreement with the world median of 0.32 μM (Meybeck and Ragu 2012). Similar to the dominance of organic forms of nitrogen,

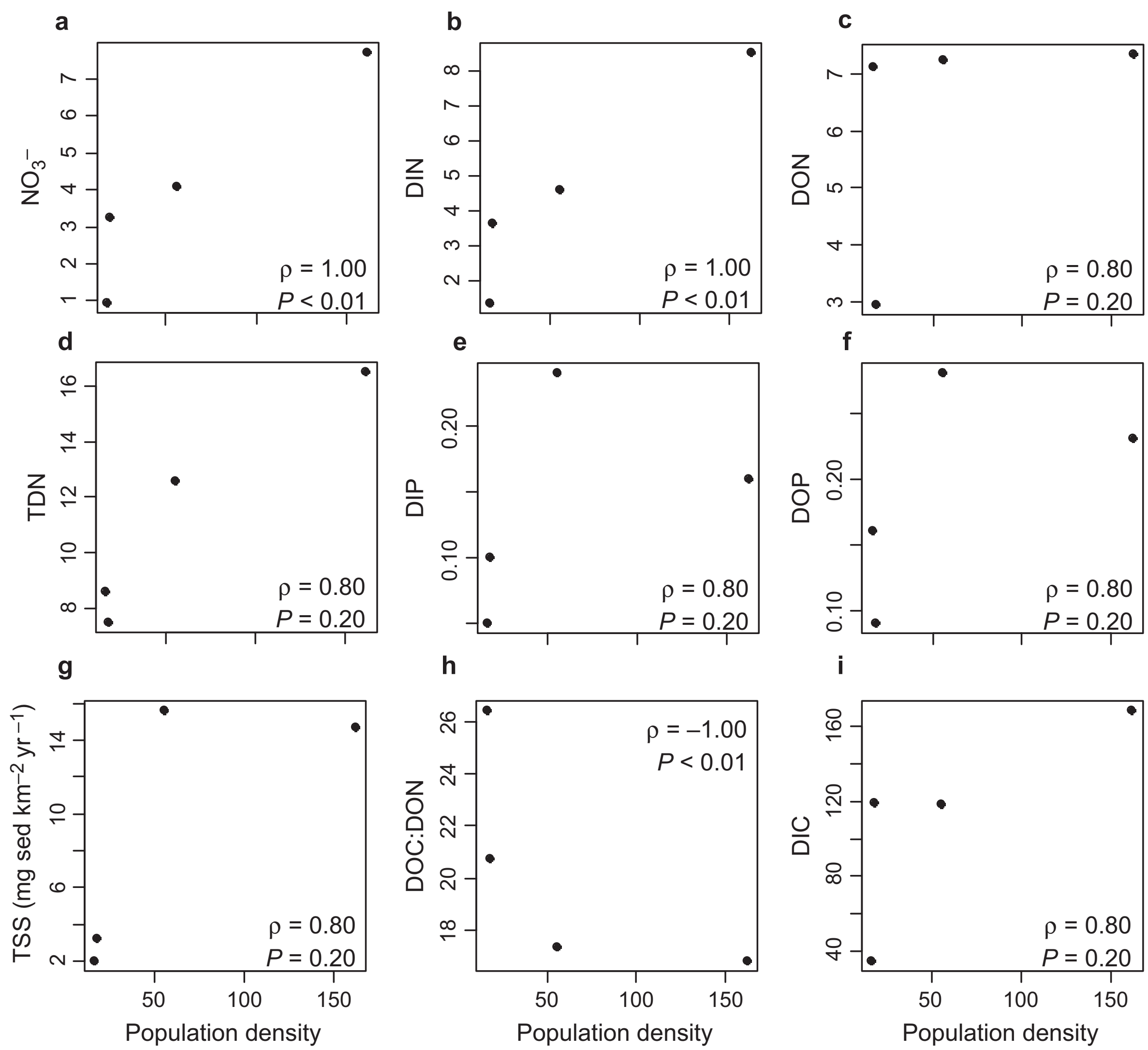

Fig. 4. Trends observed between parameter export and population density (individuals km^{-2}) across the Altamaha River Watershed (a–i). Positive or negative relationships are indicated by Spearman's rho correlation coefficient. Results were considered significant if $P < 0.05$.

DOP was the dominant P-form at all sites except for the Oconee River (Appendix S1: Table S3). The Ohoopee Tributary had the highest median DOP concentration (1.07 μM), followed by the Little Ocmulgee (0.97 μM), Ocmulgee (0.80 μM), Oconee (0.76 μM), and Altamaha (0.73 μM) rivers (Appendix S1: Table S3).

Samples from the tributaries vs. the Altamaha River indicated that annual DIP exports varied significantly (Fig. 5; Kruskal–Wallis independent test; $\chi^2 = 107.81$, df = 4, $P < 0.001$). The average annual DIP export was greatest from the Oconee River subwatershed, followed by the Ocmulgee, Ohoopee, and Little Ocmulgee subbasins, respectively. A weak positive relationship was observed between DIP and DOP export and population density within the Altamaha watershed (Fig. 4e, f). Also within the watershed, the proportion of agricultural land demonstrated a negative relationship with DIP export, while a weak positive relationship was found with livestock biomass km^{-2} (Fig. 6e, f). The Oconee River subwatershed demonstrated the greatest amount of livestock biomass (Table 5).

Table 3. A summary of the population density, proportion of agricultural land, and overall land area in the Altamaha Watershed from 1970 to 2010.

	Upper Ocmulgee	Lower Ocmulgee	Ocmulgee	Upper Oconee	Lower Oconee	Oconee	Ohoopee	Altamaha	Total
Land area (km^2)	6147	7439	13,587	7323	3953	11,276	2970	7533	35,365
Population density (km^{-2})									
1970	98	35	63	27	15	23	12	12	35
2000	238	46	133	58	19	45	15	16	70
2010	295	53	162	75	20	56	16	18	85
Agricultural land area (km^2)									
1969	2053	3456	5508	3164	1385	4549	1557	3905	15,520
2002	1208	2434	3642	2056	823	2879	1090	2623	10,233
2007	859	2228	3087	1953	765	2718	974	2396	9175
Proportion of agricultural area									
1969	0.33	0.46	0.41	0.43	0.35	0.40	0.52	0.52	0.44
2002	0.20	0.33	0.27	0.28	0.21	0.26	0.37	0.35	0.29
2007	0.14	0.30	0.23	0.27	0.19	0.24	0.33	0.32	0.26
Rate population density change ($km^2\ yr^{-1}$)									
2000–2010	5.70	0.63	2.92	1.64	0.07	1.09	0.10	0.19	1.52
1970–2010	6.56	0.60	3.30	1.59	0.17	1.09	0.14	0.20	1.67
Rate agricultural area land change ($km^2\ yr^{-1}$)									
2002–2007	−69.69	−41.19	−110.88	−20.58	−11.58	−32.16	−23.19	−45.44	−211.68
1969–2007	−31.41	−32.30	−63.71	−31.85	−16.31	−48.17	−15.36	−39.73	−166.96

Note: The Little Ocmulgee River is included in the Lower Ocmulgee sub-basin.

Carbon, silicate, and total suspended solids

The median DOC concentrations in the Little Ocmulgee and Ohoopee tributaries were 1114 and 1034 μM (Fig. 9a; Appendix S1: Table S4). These concentrations were more than two times greater than those of the Altamaha, Ocmulgee, and Oconee rivers (Kruskal–Wallis, χ^2 = 120.5, df = 4, $P < 0.0001$). DIC concentrations demonstrated an opposite pattern in which the median concentrations of the Little Ocmulgee and Ohoopee tributaries were 334 and 282 μM, almost two times lower than those of the Altamaha, Ocmulgee, and Oconee rivers (Fig. 10a; Kruskal–Wallis, χ^2 = 137.7, df = 4, $P < 0.0001$). Consequently, dissolved carbon pools in the Little Ocmulgee and Ohoopee tributaries were dominated by inorganic carbon, whereas the Altamaha, Ocmulgee, and Oconee rivers were dominated by organic carbon (Fig. 11c; Kruskal–Wallis, χ^2 = 61.9, df = 4, $P < 0.0001$).

Total suspended solids and Si distribution patterns across sites were distinct compared to DOC and DIC distributions. The TSS concentrations from 2006 to 2012 followed the following pattern: Oconee > Ocmulgee > Altamaha > Ohoopee (Fig. 9b; Appendix S1: Table S4; Kruskal–Wallis, χ^2 = 93.7, df = 3, $P < 0.0001$). The Si concentration in the Ohoopee Tributary was the lowest of all the sites (Kruskal–Wallis, χ^2 = 49.5, SD = 4, $P < 0.0001$), and there was no statistical difference in Si distribution between the Altamaha, Ocmulgee, Oconee, and Little Ocmulgee rivers (Fig. 10b; Appendix S1: Table S4).

Log–log linear regressions between parameter and discharge demonstrated that across all sites, DOC concentration significantly increased with increased discharge (Fig. 11a, Table 6). Interestingly, the sites separated into two groups (Group 1: Altamaha, Ocmulgee, and Oconee; and Group 2: Little Ocmulgee and Ohoopee). Discharge described 51% of the variation in DOC concentration in Group 1 (β_1: 0.36, df = 320, $P < 0.0001$) but only 21% in Group 2 (β_1: 0.11, df = 73, $P < 0.0001$). Similarly, the same groups separated out when DIC and discharge were plotted and statistically analyzed (Fig. 11b). Discharge described 57% of the variation in DIC concentration in Group 1 (β_1: −0.21, df = 284, $P < 0.0001$) and 25% of the variation in Group 2 (β_1: −0.06, df = 65, $P < 0.0001$). As a result, a clear separation between groups was seen when observing the behavior of the DOC:DIC ratio with discharge.

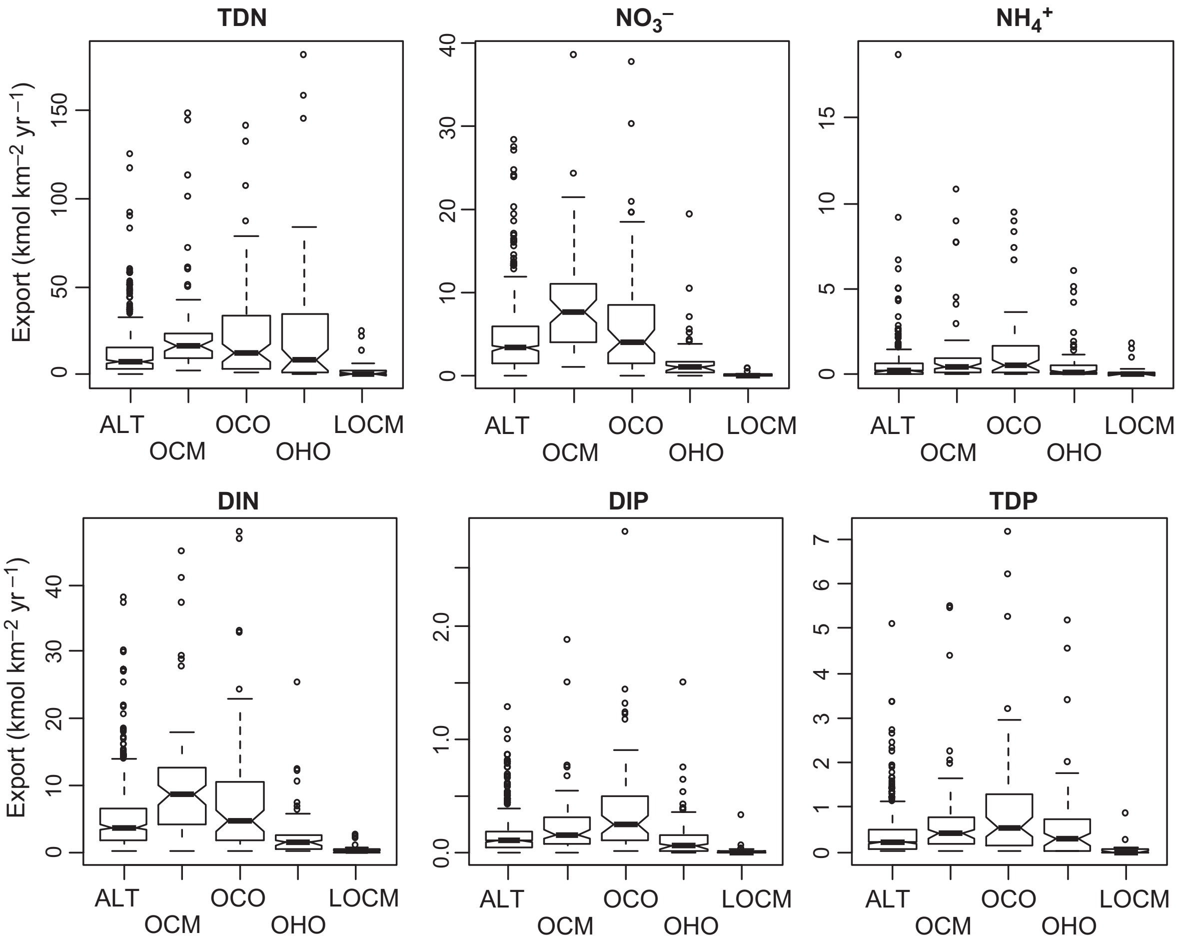

Fig. 5. A box and whisker plot summary of nitrogen and phosphorus species exports from Altamaha (ALT) and each of the tributaries in the Altamaha River Watershed from 2000 to 2012. Box indicates the interquartile range around the median; notches indicate a 95% confidence interval. Whiskers indicate the maximum and minimum values, excluding outliers. Total dissolved nitrogen (TDN), NO_3^-, and dissolved inorganic nitrogen (DIN) export was the highest from Ocmulgee (OCM; Kruskal–Wallis, $\chi^2 = 80.01, 167.75, 145.52$, df = 4, $P < 0.001$). NH_4^+ export was similar from the OCM and Oconee (OCO) rivers and higher than that from ALT, Little Ocmulgee (LOCM), and Ohoopee (OHO) rivers. Dissolved inorganic phosphate (DIP) export was significantly different between all rivers (Kruskal–Wallis, $\chi^2 = 107.81$, df = 4, $P < 0.001$). Total dissolved phosphorus (TDP) export was the highest from OCO and greater than that from ALT, OHO, and LOCM (Kruskal–Wallis, $\chi^2 = 73.23$, df = 3, $P < 0.001$).

The DOC:DIC ratio increased positively with discharge, with discharge describing 61% and 28% of the variation in Groups 1 and 2, respectively (Fig. 11d).

Across the watershed, TSS demonstrated a positive log–log relationship with discharge (Fig. 9c; β_1: 0.28, $R^2 = 0.19$, df = 454, $P < 0.0001$). The Altamaha and Oconee rivers specifically demonstrated the strongest positive relationships with TSS (Table 6; β_1: 0.25, $R^2 = 0.14$, df = 343, $P < 0.001$; and β_1: 0.38, $R^2 = 0.26$, df = 39, $P < 0.01$, respectively). Similar to DIC, Si demonstrated significant negative relationships with discharge across all sites (Table 6). Unlike DIC however, discharge only described 13–23% of the variation in Si.

To understand the potential sources of DOC and DIC, we further investigated the relationships between DOC and TSS and DIC

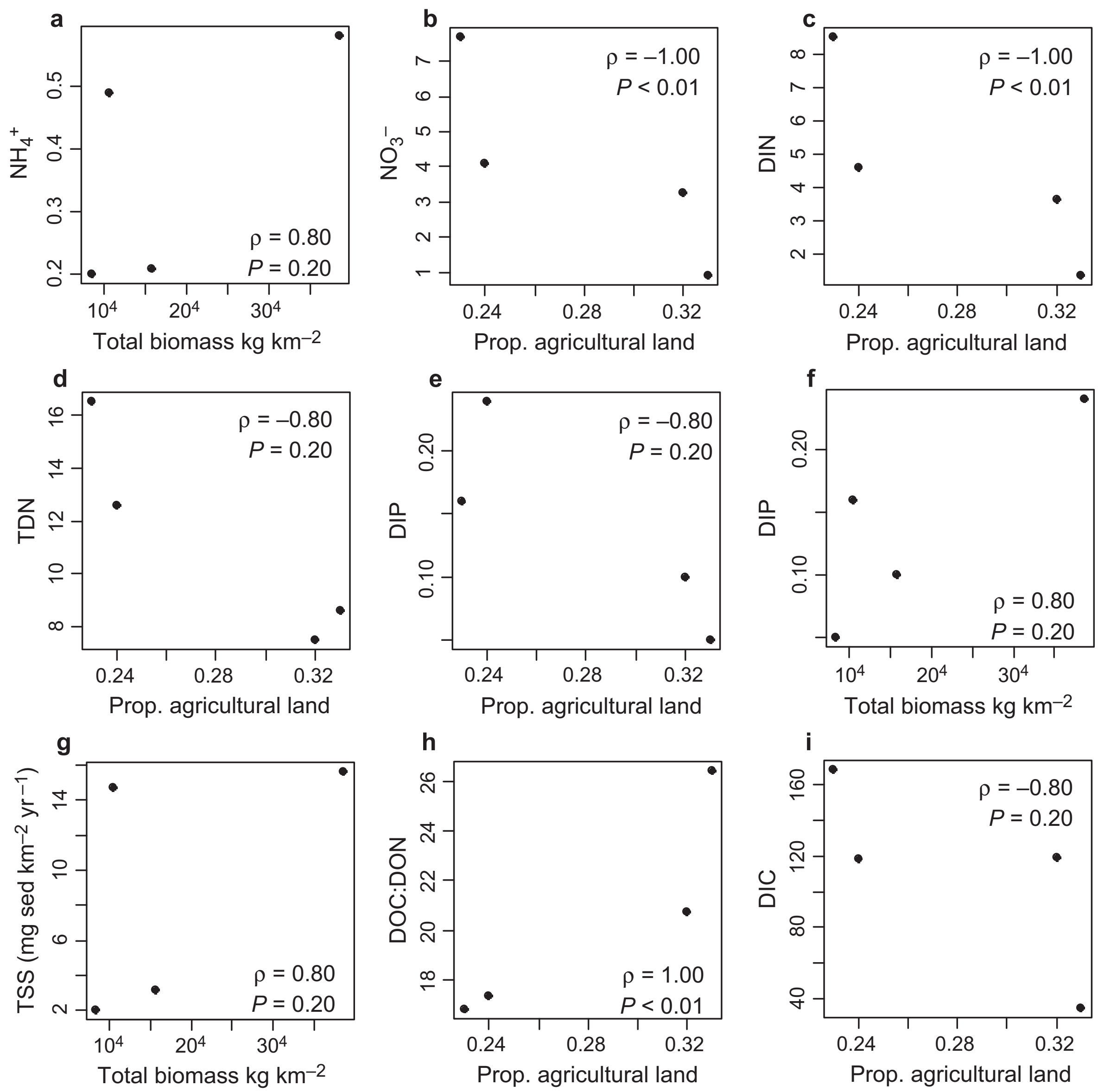

Fig. 6. Trends observed between parameter export or ratio and total livestock biomass (total biomass, kg km^{-2}; a–c), and the proportion of agricultural land (within each sub-basin) across the Altamaha River Watershed (d–i). Positive or negative relationships are indicated by Spearman's rho correlation coefficient. Results were considered significant if $P < 0.05$.

and Si. Log–log regressions of DOC vs. TSS revealed that TSS described 12%, 19%, and 34% of the variation in DOC concentrations in the Altamaha, Ocmulgee, and Oconee rivers, respectively (Fig. 9d–f). When DIC and Si were regressed against each other, a significant positive relationship was observed in the Altamaha, Ocmulgee, and Oconee rivers combined (Group 1), but not in the Ohoopee and Little Ocmulgee rivers (Group 2). The Si concentrations in the Altamaha, Ocmulgee, and Oconee rivers explained 13% of the variation in DIC (Fig. 10c; β_1: 0.31, df = 194, $P < 0.0001$).

Potential sources of DOC, DIC, Si, and TSS within the entire watershed were further explored by comparing estimated annual exports with the

Table 4. A summary of the simple log–log linear regressions describing the variance of each phosphorus parameter (concentration, μM, or ratio): dissolved organic phosphorus (DIP), dissolved organic phosphorus (DOP), DIN:DIP, DOP:DIP, and TDN:TDP as described by discharge.

Site	DIP	DOP	TDP	DIN:DIP	DOP:DIP	TDN:TDP
Altamaha						
β_1	−0.178	0.223	0.025	0.114	0.396	−0.006
R^2	0.055	0.092	0.003	0.014	0.121	0.000
P-value	**<0.001**	**<0.001**	0.220	**0.007**	**<0.001**	0.764
df	523	505	511	518	505	506
Oconee						
β_1	−0.088	0.190	0.073	0.086	0.234	−0.016
R^2	0.021	0.112	0.046	0.013	0.067	0.002
P-value	0.229	**0.007**	0.089	0.339	**0.040**	0.751
df	69	61	62	68	61	62
Ocmulgee						
β_1	−0.151	0.220	0.068	−0.113	0.362	−0.096
R^2	0.028	0.076	0.018	0.018	0.078	0.034
P-value	0.154	**0.021**	0.258	0.267	**0.019**	0.124
df	72	68	70	70	68	69
Little Ocmulgee						
β_1	0.026	0.024	0.003	0.069	0.017	0.105
R^2	0.007	0.004	0.000	0.029	0.001	0.116
P-value	0.671	0.762	0.953	0.406	0.875	0.103
df	26	22	22	24	22	22
Ohoopee						
β_1	−0.186	0.017	−0.046	−0.125	0.183	0.092
R^2	0.218	0.001	0.032	0.055	0.077	0.127
P-value	**<0.001**	0.767	0.140	0.051	**0.024**	**0.003**
df	69	64	67	68	64	67

Note: The *P*-values in bold indicate the slope of the relationship is significantly different from zero ($P < 0.05$).

proportion of agricultural land, population density, and livestock density. Although not significant, DOC demonstrated a negative relationship with livestock biomass (data not shown). TSS export demonstrated strong, significantly positive relationships with population density and livestock biomass (Figs. 4g and 6g). When compared to the proportion of agriculture however, a negative relationship was observed (data not shown). DIC and Si export demonstrated the same negative relationship (Si, not shown; DIC, Fig. 6i). Similar to TSS, a strong positive relationship with population density was also observed with both Si and DIC (Si, not shown; DIC, Fig. 4i).

N:P ratio

The median TDN:TDP and DIN:DIP ratios and interquartile ratios are presented in Appendix S1: Table S3. When only the inorganic forms of N and P were considered, the Ocmulgee River had the highest overall DIN:DIP ratio (DIN:DIP = 50). According to the 16:1 Redfield ratio that reflects phytoplankton nutrient uptake ratios (Chapin III et al. 2002), the river was strongly P-limited. This was followed by a significantly lower DIN:DIP ratio in the Altamaha (median DIN:DIP = 36, Kruskal–Wallis, $\chi^2 = 55$, df = 4, $P < 0.0001$). The lowest DIN:DIP ratios demonstrated similar median values and distributions in the Oconee, Ohoopee, and Little Ocmulgee tributaries (median range: 18–23). However, if both the inorganic and organic fractions of N and P were considered in the TDN:TDP ratio, the patterns between rivers were different. The Little Ocmulgee Tributary instead had the highest median ratio (TDN:TDP = 43), followed by the Ocmulgee, Ohoopee, Altamaha, and Oconee rivers. In the Altamaha and Ocmulgee rivers, the addition of the organic forms of N and P decreased the estimated N:P ratio (36 to 31, and 50 to 40, respectively). In the Oconee, Ohoopee, and Little Ocmulgee rivers however, the change was the opposite. The consideration of the organic forms of N and P increased the N:P ratio (18–25, 23–33,

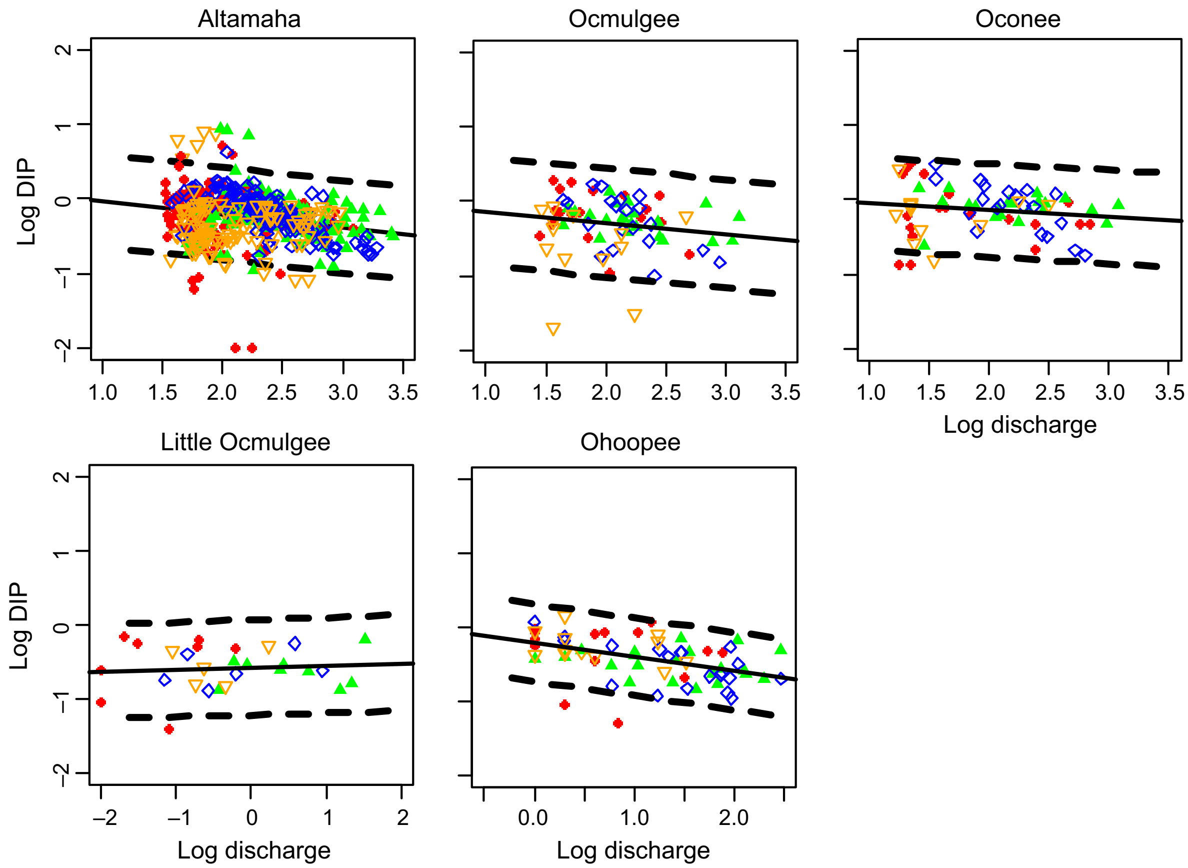

Fig. 7. Log–log regressions comparing the relationship between dissolved inorganic phosphorus (DIP) concentration and discharge in the Altamaha, Ocmulgee, Oconee, Little Ocmulgee, and Ohoopee rivers. Color and symbols indicate different seasons. Red circles represent fall, blue diamonds represent winter, green triangles represent spring, and orange triangles represent summer. The solid line is the plotted log–log linear regression, and the dashed lines indicate 95% confidence interval.

and 22–43, respectively). These results are addressed further in the *Discussion*.

Comparisons between DIN:DIP ratio and discharge demonstrated a slight, positive slope in the Altamaha River (Table 4). When the TDN:TDP ratio was considered, there was a similarly slight, positive increase with discharge in the Ohoopee River ($\beta_1 = 0.09$, $R^2 = 0.13$, $P < 0.01$). When the DIN:DIP or TDN:TDP ratios were log–log-regressed against discharge at all other sites, the slope did not significantly differ from zero (Table 4).

C:N ratio

The median values and interquartile ranges of DOC ratio with DIN, DON, and TDN are presented in Appendix S1: Table S4. Kruskal–Wallis comparisons (and post hoc Mann–Whitney *U* tests) of the median DOC:DIN ratios in the Altamaha watershed showed that the Little Ocmulgee had the highest ratio (DOC:DIN = 147), followed by the Ohoopee (89), Oconee (26), Altamaha (22), and Ocmulgee (15) rivers, respectively ($\chi^2 = 145.4$, df = 4, $P < 0.0001$). A similar trend was noted with the DOC:TDN ratio; however, in this comparison, the distributions in the Little Ocmulgee and Ohoopee tributaries were not significantly different from each other ($\chi^2 = 123.0$, df = 4, $P < 0.0001$). It is interesting to note that when only the organic fractions of C and N are compared, across the watershed, the ratios are similar. With the exception of the Ohoopee River (DOC:DON = 26), all sites had a DOC:DON ratio <25.

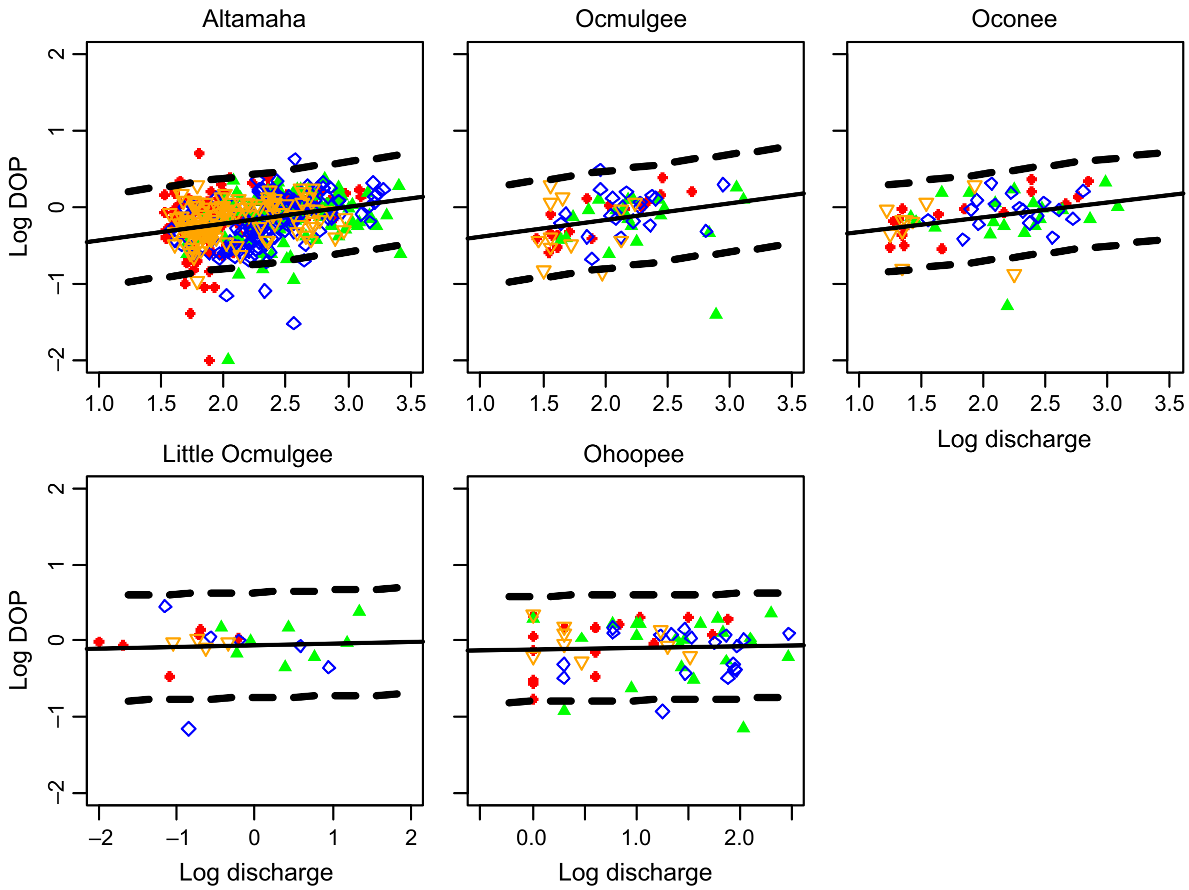

Fig. 8. Log–log regressions comparing the relationship between dissolved organic phosphorus (DOP) concentration and discharge in the Altamaha, Ocmulgee, Oconee, Little Ocmulgee, and Ohoopee rivers. Color and symbols indicate different seasons. Red circles represent fall, blue diamonds represent winter, green triangles represent spring, and orange triangles represent summer. The solid line is the plotted log–log linear regression, and the dashed lines indicate 95% confidence interval.

The results of the log–log regressions of the DOC:N ratios vs. discharge are presented in Table 6. With the exception of the Little Ocmulgee Tributary, the DOC:DON, DOC:TDN, and DOC:DIN ratios demonstrated significant positive relationships with discharge at all sites ($P < 0.05$). The DOC:DON ratio across the watershed demonstrated a strong, significantly positive relationship with the proportion of agricultural land (Fig. 6h) and a significant

Table 5. Summary of the recorded livestock density (cattle, hogs, and chickens) in the Altamaha Watershed for each subwatershed based on the 2007 Agricultural Census, normalized by biomass.

	Upper Ocmulgee	Lower Ocmulgee	Ocmulgee	Upper Oconee	Lower Oconee	Oconee	Ohoopee	Altamaha	Total
Livestock									
kg cattle km^{-2}	3330	2986	3141	8875	2395	6604	3530	3301	16,576
kg hogs km^{-2}	3	15	10	142	11	96	100	25	231
kg chickens km^{-2}	5180	9186	7374	47,698	2556	31,874	4783	12,413	56,444
Total kg livestock km^{-2}	8513	12,187	10,525	56,715	4962	38,574	8414	15,739	73,251

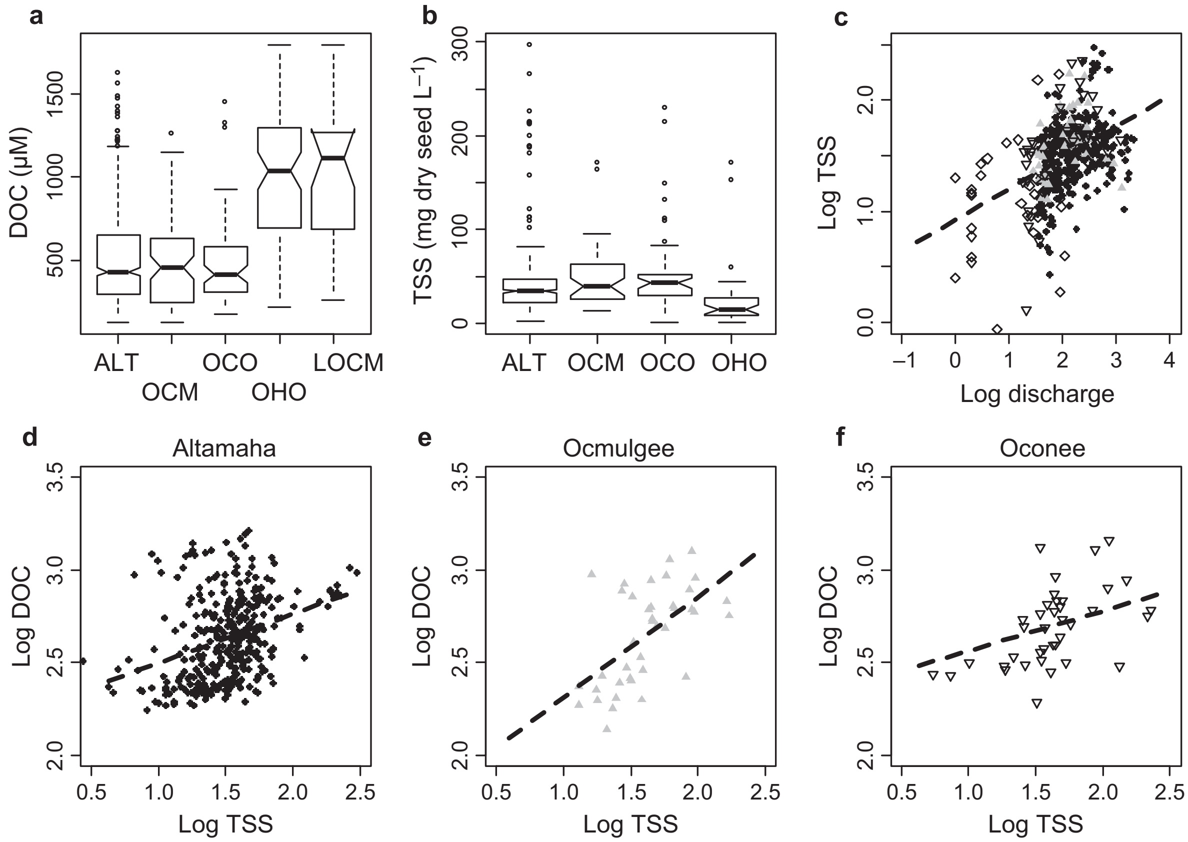

Fig. 9. Comparisons of dissolved organic carbon (DOC) and total suspended solids (TSS). (a) Box and whisker plot of DOC concentrations at each site from 2000 to 2012. (b) Box and whisker plot of TSS collected from 2006 to 2012. (c) Log–log regression of TSS and discharge across the Altamaha Watershed. (d–f) Log–log regression assessing relationship between DOC and TSS in the Altamaha, Ocmulgee, and Oconee rivers. Filled circles represent the Altamaha, open triangles represent the Oconee, filled triangles represent the Ocmulgee, and open diamonds represent the Ohoopee River.

negative relationship with population density (Fig. 4h).

Drivers of discharge

A comparison of the average monthly precipitation across the state of Georgia, averaged over 30-year increments, indicated that over the last 80 years, the driest months of the year have shifted from October and November to April and May (Appendix S1: Fig. S1). From 1990 to 2012 alone, the precipitation in October and November increased by 11.5% and 6.2% with respect to the previous 60 yr (November, Kruskal–Wallis, $\chi^2 = 7.10$, df = 2, $P < 0.05$). In contrast, the total precipitation in April and May decreased by 21% and 16%. Summer rainfall in July decreased, averaging 148.7 mm from 1900 to 1929, and falling to 125.8 mm from 1990 to 2012 (SERCC; Kruskal–Wallis, $P = 0.06$). While average yearly rainfall has remained relatively constant, it should be noted that from 1990 to 2012, the average rainfall was 5% less than the average rainfall of the previous 90 yr (SERCC). Taken together, although the average total annual precipitation has not changed dramatically in the last 100 years, the timing of the dry and wet seasons has shifted.

This variation in climate is further demonstrated in the historical discharge patterns of the Ocmulgee, Oconee, and Altamaha rivers (Appendix S1: Fig. S2). Similar to the change in precipitation patterns, a comparison between the historical monthly average discharges indicates

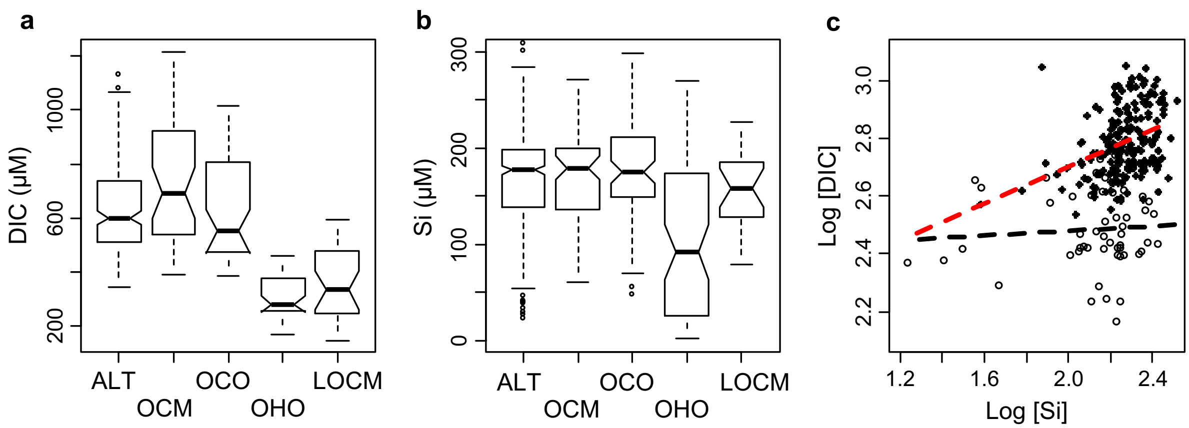

Fig. 10. Comparisons of dissolved inorganic carbon (DIC) and silicate (Si). (a) Box and whisker plot of DIC concentrations at each site from 2000 to 2006. Box indicates the interquartile range around the median; notches indicate 95% confidence interval. Whiskers indicate the maximum and minimum values, excluding outliers. (b) Box and whisker plot of silicate concentrations, and (c) log–log regression assessing the relationship between DIC and Si across the Altamaha Watershed. Group 1, represented by closed circles, are the Altamaha, Oconee, and Ocmulgee rivers; and Group 2, represented by open circles, are the Ohoopee and Little Ocmulgee rivers.

a dramatic decrease during April and May from 2000 to 2012 in comparison with the same months from 1932 to 1952 (Appendix S1: Fig. S2a–c). Further assessment of the changes in flow from 2000 to 2012 indicates that the Oconee River flow has decreased the most dramatically with a greater than 40% decrease in January, February, May, and August as compared to the previous 70-yr averages (Appendix S1: Fig. S2b). The impacts of these changes were further observed in the flow-duration curves of the Altamaha, Ocmulgee, Oconee, and Ohoopee rivers (Appendix S1: Fig. S3). The Ohoopee River had the steepest slope, whereas the slope of the Ocmulgee flow-duration curve was the most shallow. The Altamaha and Oconee rivers had similar slopes.

Since 1970, the Ocmulgee and Oconee River subwatershed populations have increased at a rate of 3.3 and 1.1 individuals $km^{-2}\,yr^{-1}$, respectively (Table 3), whereas the populations in the Ohoopee and Altamaha River sub-basins have increased at a rate of 0.14 and 0.20 individuals $km^{-2}\,yr^{-1}$, respectively. In the last decade alone however, the Ocmulgee River sub-basin had the greatest increase in population density, at a rate of 3 individuals $km^{-2}\,yr^{-1}$, specifically in the Upper Ocmulgee River sub-basin where the population increase rate was 6 individuals $km^{-2}\,yr^{-1}$ (Appendix S1: Fig. S4a). In contrast to the population increases, the proportion of land used for agriculture has decreased in all sub-basins since 1969 (Table 3). The largest rate of decrease has been in the Ocmulgee River Basin, which has lost, on average, 64 $km^2\,yr^{-1}$ of agricultural land since 1969. From 2002 to 2007 alone, the Upper Ocmulgee River sub-basin reported the most dramatic decrease in agricultural land area at close to 70 $km^2\,yr^{-1}$.

A comparison of the average flow of the Altamaha River and its tributaries (from 2000 to 2012) indicates the highest overall flows occur in the winter (December–February) and early spring (March–April; Appendix S1: Fig. S5a). The Altamaha River has the highest average flow throughout the year. The Ocmulgee and Oconee tributaries have similar flows, and the lowest average flows were observed in the Ohoopee and Little Ocmulgee tributaries. If we assume that the flow of the Altamaha is the cumulative result of its major tributaries, we can compare the average percent contribution of each tributary to the overall flow of the Altamaha River. We calculated this using discharge data from each tributary and the Altamaha River from 2000 to 2012 (Appendix S1: Fig. S5b). These patterns indicate that the contribution of the Ocmulgee and Oconee rivers to the flow of the Altamaha River varies depending on the time of year.

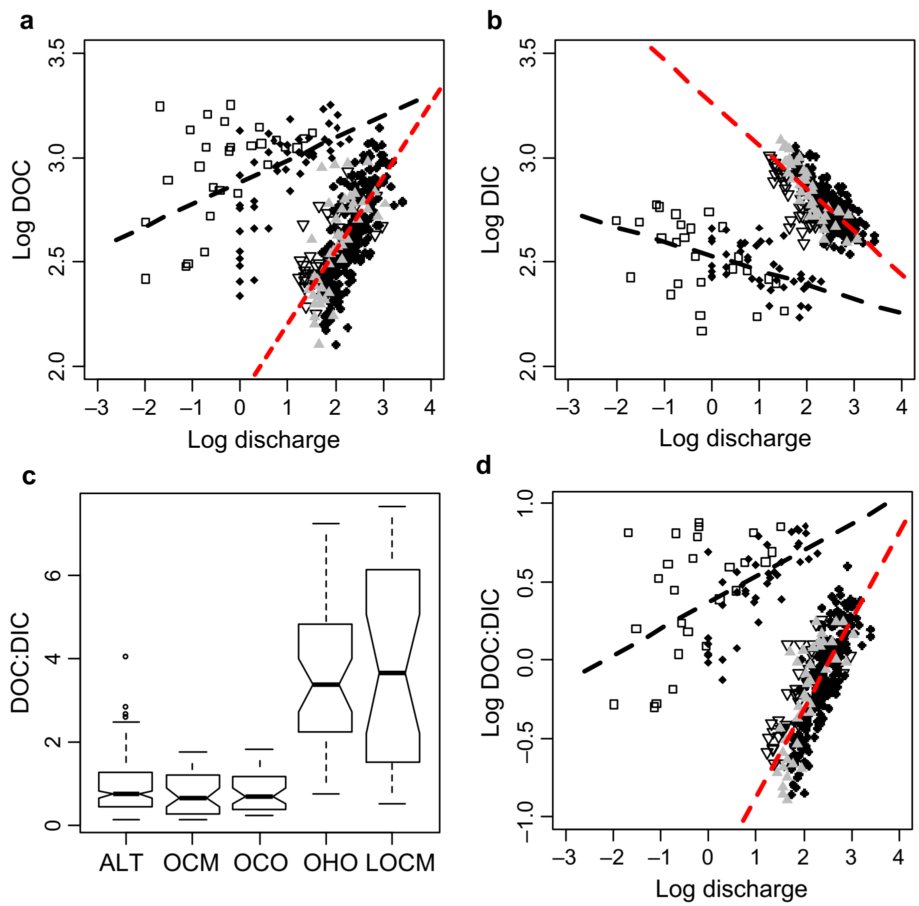

Fig. 11. Comparisons between dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and discharge: Different carbon dynamics are seen between sites. The relationship between carbon in the Altamaha (ALT), Ocmulgee (OCM), and Oconee (OCO) rivers with discharge is depicted with red dashed lines, and the relationship between carbon in the Little Ocmulgee (LOCM) and Ohoopee rivers (OHP) is depicted with black dashed lines (a, b, and d). (c) A comparison of DOC:DIC means across sites. Filled circles represent the Altamaha, open triangles represent the Oconee, filled triangles represent the Ocmulgee, filled diamonds represent the Ohoopee, and open squares represent the Little Ocmulgee River.

During higher flow periods (January through April), the two tributaries demonstrate an equal contribution. During low-flow periods (May through August), the Ocmulgee Tributary has a higher overall contribution to the Altamaha flow, whereas during September through December, both flow and the relative contribution of the Ocmulgee and Oconee rivers are the most variable. In general, the Ohoopee River contributes to less than 20% of overall flow, while the Little Ocmulgee contributes less than 5%. Interestingly, the cumulative contributions of the four tributaries into the Altamaha ranged from 60.3% to 131%. These results are further addressed in the *Discussion*.

Given that the contribution of each tributary to the overall flow of the Altamaha River demonstrated seasonal patterns, we investigated how these contributions changed under periods of low flow (seasonal dry periods and drought) as well and during periods of high flow (seasonal rainy periods and floods). The exceedance value percentages used are in accordance with the percentages used by USGS to indicate low flow ("dry," P25), normal flow ("median," P50), and high flow ("flood," P75). The historical flow

Table 6. A summary of the simple log–log linear regressions describing the variance of each carbon, silicate, and total suspended solids (TSS) parameters: dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), silicate (Si), TSS, DOC:DON, DOC:TDN, DOC:DIN, and Si:DIN as described by discharge.

Site	DOC	DIC	DOC:DIC	Si	TSS	DOC:DON	DOC:TDN	DOC:DIN	Si:DIN
Altamaha									
β_1	0.288	−0.243	0.682	−0.141	0.250	0.096	0.269	0.357	−0.109
R^2	0.303	0.672	0.689	0.132	0.135	0.028	0.229	0.120	0.015
P-value	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**0.010**
df	524	202	198	441	340	516	519	519	437
Oconee									
β_1	0.225	−0.199	0.450	−0.146	0.382	0.132	0.174	0.186	−0.236
R^2	0.356	0.589	0.641	0.186	0.256	0.124	0.199	0.060	0.076
P-value	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**0.001**	**0.002**	**<0.001**	**0.035**	**0.025**
df	73	39	38	65	37	72	72	72	64
Ocmulgee									
β_1	0.396	−0.295	0.676	−0.151	0.185	0.207	0.470	0.645	0.076
R^2	0.410	0.771	0.638	0.134	0.072	0.087	0.417	0.386	0.012
P-value	**<0.001**	**<0.001**	**<0.001**	**0.002**	0.099	**0.012**	**<0.001**	**<0.001**	0.383
df	72	39	38	66	37	69	71	70	64
Little Ocmulgee									
β_1	0.120	−0.098	0.210	−0.067	–	0.025	0.006	0.018	−0.171
R^2	0.235	0.257	0.259	0.228	–	0.070	0.004	0.002	0.131
P-value	**0.009**	**0.008**	**0.008**	**0.033**	–	0.191	0.765	0.819	0.128
df	26	24	24	18	–	24	26	24	17
Ohoopee									
β_1	0.216	−0.085	0.302	−0.321	0.191	0.071	0.183	0.541	−0.003
R^2	0.529	0.294	0.599	0.180	0.086	0.163	0.500	0.562	0.000
P-value	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.083	**<0.001**	**<0.001**	**<0.001**	0.972
df	72	39	39	64	34	72	72	71	63

Note: The *P*-values in bold indicate the slope of the relationship is significantly different from zero ($P < 0.05$).

data for the Altamaha River from 1932 to 2012 were used as a reference, and the percent contribution of each tributary during times when the Altamaha River exhibited each flow class was calculated. Using the flow data compiled from the common sample days within the study period (Appendix S1: Fig. S6) shows that the dominant contributor to the Altamaha River is the Ocmulgee River (contributing an average of ~60% of the flow) during times of low flow (i.e., dry conditions), especially during the summer season. The Oconee River can have a greater contribution to flow during major flood events and during the winter season; however, an increase in flow regime also increases the variability of the contribution of the Oconee River.

Discussion

Nitrogen dynamics

Geologic factors could contribute to naturally high N-concentrations in the Altamaha River Watershed. The loamy and clayey soils in the Piedmont Province vs. the sandy Coastal Plain Province (Jordan et al. 1997) could explain the higher median NO_3^- concentrations in the Oconee and Ocmulgee tributaries than in the Little Ocmulgee and Ohoopee tributaries. The Upper Ocmulgee and Oconee tributaries lie in the Piedmont Province, and the Ohoopee and Little Ocmulgee tributaries lie almost exclusively in the Coastal Plain Province (Georgia EPD 1998, 2004*a*, *b*). This implies that groundwater flow paths and lack of NO_3^- uptake from the underlying geology of the upper tributaries vs. uptake by riparian forests in the Coastal Plain are likely contributing factors to the N-inputs into the watershed. However, further analyses of these data suggest that anthropogenic factors likely have a higher impact on driving N-inputs into the Altamaha River Watershed.

This is first demonstrated in the comparison of our data to regional, national, and global N-concentration averages. The USGS estimates that the background concentrations of nutrients in streams and groundwater of the United States are 3.9 μM for NO_3^- and 41.4 μM for total nitrogen (Dubrovsky et al. 2010). According to the Georgia EPD, NO_3^--N concentrations below 1 ppm (16.1 μM) are considered unpolluted (Georgia EPD 2015). Furthermore, Meybeck (1982) established that world rivers average >0.4–1.98 μM. The median NO_3^- concentration in the Altamaha and Ocmulgee rivers was 20.2 and 28.0 μM, respectively. The median TDN concentrations in each tributary and the Altamaha ranged from 44.5 to 57.9 μM. These numbers alone indicate a high likelihood that N-concentrations in the Altamaha Watershed are impacted by anthropogenic inputs.

Our initial hypothesis predicted a strong relationship between DIN (specifically ammonium) and livestock. This was based on the proportion of each county in each watershed (United States Department of Agriculture 2009, Weston et al. 2009), which indicated that the Oconee River subwatershed has the greatest amount of livestock, particularly broiler chickens (Table 5; Appendix S1: Table S5). Using the potential livestock excretion loads from Van Horn (1998), we calculated that if nitrogen exports were primarily influenced by livestock biomass, the Oconee River subwatershed would have the greatest N-export (Appendix S1: Table S5). The weak positive relationship observed between ammonium export and livestock confirms that livestock biomass contributes to the N-dynamics in the Altamaha Watershed. However, the stronger positive relationship between nitrate export and population density indicates that population is more likely a major factor driving N-export. This is demonstrated in the Ocmulgee River, which had the highest population density and the highest N-export (Fig. 5).

The high DIN concentrations in the Ocmulgee River could be further compounded by the evidence that N-exports are highly dependent on the amount of NO_3^- input to the soils as a result of agricultural use and other sources (Howarth et al. 1996, Jordan et al. 1997). However, the significant negative relationship between NO_3^- and DIN annual export and the proportion of agricultural, respectively (Fig. 6b, c), contrasted with the significant positive relationships observed with population density (Fig. 4a, b). These results further indicate that N-dynamics are more strongly driven by population increases than by land use allocation.

DON is the dominant N-form in the TDN export in all tributaries (with the exception of the Little Ocmulgee). All the tributaries and the Altamaha River showed a positive log–log relationship between DON concentration and discharge, indicating that with increased discharge, the rivers export more DON than they receive. Given the relationship between DON export and population density, it is possible that part of the DON input into the watershed is as a result of anthropogenic sources (i.e., storm water runoff from urban and suburban and agricultural areas; Seitzinger et al. 2002). This is interesting as global surveys have indicated that the N-pool is primarily dominated by NO_3^-, which makes up an average of 77% (Meybeck 1982). In this study, DON makes up between 47% and 88% of the TDN pool. While these proportions are in relative agreement with a study conducted on the various geologic provinces underlying the Potomac River Basin (Liu et al. 2000), they contrast with other locations around the globe (Turner et al. 2003, Ludwig et al. 2009). This underscores the importance of considering regional geology and latitude on what influences nutrient dynamics in river basins (Liu et al. 2000, Turner et al. 2003, Meybeck and Ragu 2012).

The role of regional specificity on watershed nutrients is also evident in hydrologic dynamics. The shallow slopes ($-0.5 < \beta_1 < 0.5$) observed in the log–log regressions of each N-form, specifically TDN, against discharge indicate that the main factor driving N-dynamics in the Altamaha Watershed is hydrology. This suggests that despite higher-than-average N-concentrations on a watershed scale, the tributaries and the Altamaha River are chemostatic. The between-site variability observed in N-patterns suggests that the mechanisms governing the biogeochemical balance of N differ depending on the subwatershed. For example, in the Oconee and Ohoopee tributaries, the overall movement of N is most strongly based on hydrologic flow. This implies that increased flow will increase the net amount of N transported into the Altamaha River, particularly as DON and NH_4^+ from the Oconee River. In contrast, the Ocmulgee Tributary demonstrated strong dilutions of N-forms (specifically

NO_x) with increased flow. Thus, despite having the highest N-concentrations, the Ocmulgee Tributary exported relatively lower DIN concentrations with increased flow.

The Oconee River is the most similar to the Altamaha. In these two systems, N-exports were driven by water volume as a result of increased precipitation and discharge. The times in which the DIN concentrations in the Oconee River were similar to those in the Altamaha were June 2002 and June and July 2006. These conditions occurred during prolonged dry conditions (i.e., the previous 2 months had less-than-average rainfall) and could also be indicative of increased N-loss via denitrification across the entire watershed. Interestingly, one instance in which TDN concentrations were conspicuously low in the Altamaha River was September 2010. At this time, the Oconee also had a lower-than-expected TDN concentration and the Ocmulgee had a lower-than-expected DON concentration. Both conditions may have contributed to the overall lower TDN concentration in the Altamaha River.

The Ohoopee River demonstrated dilution of DIN (NO_3^- and NH_4^+ specifically) with an increase in discharge. However, the overall TDN was driven by water volume as a result of hydrologic conditions. The dominant N-form was also DON. This suggests that unlike the Ocmulgee River, the Ohoopee River N-dynamics were likely driven by consistent terrestrial inputs from the surrounding forest (e.g., groundwater input) and leaching.

The Little Ocmulgee Tributary was the only tributary to demonstrate an increase in TDN content as a result of increased discharge. This suggests that the N-concentrations in the Little Ocmulgee are most influenced by external inputs as a result of runoff. While increased precipitation and discharge will increase the amount of N exported into the Altamaha River, the net amount is less important to the whole watershed as this tributary contributes less than 5% of the overall flow of the Altamaha.

Whole-watershed N-implications

Previous studies assert that DIN removal becomes less efficient during flood events (despite an increase in N-export); however, the chemostatic nature of the Altamaha Watershed suggests otherwise (Inwood et al. 2007, Mulholland et al. 2008, Alexander et al. 2009). Our results show that the watershed has a high buffering capacity to cope with climatic disturbances such as those resulting in increased discharge and subsequently increased nutrient exports. Despite the often higher-than-expected DIN (NH_4^+, NO_3^-, or NO_2^- individually or cumulatively) or DON concentrations with increased flow, the overall TDN concentrations were consistent with the chemostatic model. At times even, increased flow decreased N-concentrations, as seen in the NO_3^- concentrations in the Ocmulgee and Ohoopee rivers.

We propose two separate mechanisms to explain this. The N-retention mechanism under low-flow conditions is physically and biologically driven by increased residence times and increased nutrient processing efficiency of the ecosystem. This is evidenced in the lower-than-expected DIN concentrations observed primarily during times of low-flow and "dry" precipitation conditions. Nitrogen retention under high-flow conditions, despite a decrease in nutrient processing (and increased export), is more physically driven by a lower volume of water exported out of the lower watershed relative to the upper watershed, likely due to overflow into the extensive floodplains and the gently sloping geomorphological characteristics of the Coastal Plain (slopes average ~0.35 m km^{-1}, Georgia EPD 2004*a*). In the context of climate change however, these data indicate that the Altamaha Watershed N-cycle will be the most strongly affected during conditions of low flow and decreased precipitation, compounded by warm, seasonal temperatures (summer and early fall). These are the most likely times in which exceptional N-removal could occur.

Given the above evidence that the flow and nutrient inputs into the Altamaha River Watershed are strongly impacted by anthropogenic influences and that DON is the dominant form of exported N-species, additional research is necessary to determine both the anthropogenic sources of DON and the extent of its impact on the watershed ecosystem dynamics. This is a subject of further interest as global surveys generally indicate that inorganic nitrogen (specifically NO_3^-), not DON, dominates the N-pool in rivers (Turner et al. 2003, Ludwig et al. 2009). While some studies have assessed the bioavailability of DON, fewer studies have assessed its ecological impact when it is the dominant N-form. Berman and Bronk (2003) concluded that the composition of the DON pool in aquatic systems could be less recalcitrant and more bioavailable than originally thought. The possibility of DON as a biologically available N-form is further evident in the fact that our results show that in general, DON concentrations are lower than expected during the fall, winter, and spring seasons of drier years—which are exactly the times in which DIN concentrations are not lower than expected.

Phosphorus dynamics

The lack of a log–log relationship between TDP and discharge indicates that the P-dynamics in the Altamaha River Watershed are chemostatic, thus demonstrating that the amount of phosphorus exported from the system is primarily controlled by hydrology. The percent contributions of DIP to the overall P-pool (44–46%) in the ALT, OCO, and OCM are similar to world averages (40–46%; Meybeck 1982, Turner et al. 2003, Meybeck and Ragu 2012). The median PO_4^{3-} concentration in world rivers is 0.32 μM, and the average TDP concentration is 6.0 μM (Meybeck and Ragu 2012). The background PO_4^{3-} and TDP concentrations in U.S. rivers are 0.11 μM and 1.1 μM, respectively (Dubrovsky et al. 2010), and the Georgia EPD Adopt-A-Stream Manual states that total phosphorus levels greater than 0.1 ppm (3.2 μM) indicate potential human sources are present (Georgia EPD 2015). In this study, the median DIP and TDP concentrations found in this study were 0.78 μM and 1.5 μM. These results imply that while TDP may not be heavily influenced by anthropogenic influences, DIP likely is.

Similar to the N-dynamics, the percent contributions of DOP (54–77%) are well above those of previous studies. Liu et al. (2000) estimated a 37% contribution in the Coastal Plain Province and a 27% contribution in the Piedmont Province. While overall TDP concentrations were lower than the world averages, the dominance of DOP, the relationships found between P-forms and livestock biomass and population density, and the higher-than-average DIP concentrations all indicate that the P-dynamics in the Altamaha River Watershed are influenced by anthropogenic sources.

The delivery of natural and anthropogenic phosphorus into watersheds varies depending on source and time of year. Both organic and inorganic phosphorus forms derive from natural weathering and erosion, organic matter decomposition, leaf litter, industrial effluent, fertilizers, residential activities, domestic animal excreta, detergents, and lubricants (Withers and Jarvie 2008, Georgia EPD 2015), all of which are potential P-inputs into the Altamaha Watershed. Once delivered to the system, P-fluxes and transformations are controlled by biological, physical, and chemical processes exemplified by the following: uptake and release by biota and sediments, adsorption and desorption onto sediment surfaces, precipitation and dissolution, and movement of pore water through streambeds (House 2003, Withers and Jarvie 2008). Phosphorus bioavailability within the riverine ecosystem is further dependent on the source, speciation, and solubilization in water (Withers and Jarvie 2008, Darch et al. 2014). DIP is considered the most readily available form of P metabolized by algae, plants, and microbes (Caraco 1995, Howarth et al. 1996), whereas DOP is considered less bioavailable. However, it is clear that some fraction of the DOP pool is bioavailable (Correll 1998, Darch et al. 2014).

In the Altamaha Watershed, previous studies indicated that water–sewage treatment runoff, proximity to dairy and poultry operations, and fertilizer inputs all highly contribute to the P exported into these rivers (Fisher et al. 2000, Romeis and Jackson 2005, Schaefer and Alber 2007). The results of this study indicate that the major anthropogenic sources of P-inputs are likely livestock biomass and population density. This agrees with previous studies which have shown that 47% of P loading into the surface water of watersheds are a result of P-losses (as feces) from livestock (Knowlton et al. 2001, Orr et al. 2011) and that further P-inputs are highly influenced by urbanization and population increases (Caraco 1995, Fitzpatrick et al. 2007, Weston et al. 2009). This is evident in our calculations which predicted the contribution of the Oconee River sub-basin to be the greatest due to its high livestock density (Appendix S1: Table S5). This conclusion is further supported by the positive trends observed between population density and livestock biomass with DIP and DOP export (Figs. 4e, f and 6f) and the result that the Oconee subwatershed also demonstrated the highest overall DIP and TDP exports (Fig. 5).

Under undisturbed conditions, the abiotic controls on phosphorus export are primarily runoff and rainfall. In particular, up to 74% of the total phosphorus exported was the particulate form, as a result of weathering and erosion (Chapin et al. 2002, Rodríguez-Blanco et al. 2013). Although analyses of particulate phosphorus were beyond the scope of this study, the slight yet significant increases observed in DOP concentrations with discharge in the Altamaha, Oconee, and Ocmulgee rivers imply the contribution of leached organic P-forms into the watershed as a result of increased discharge (Monbet et al. 2008). The negative relationship observed between DIP and discharge in the Altamaha and Ohoopee rivers suggests DIP concentrations were likely the result of internal inputs (e.g. groundwater advection through streambed sediments) as opposed to runoff and precipitation. This explains the dilution of DIP concentrations with increased discharge.

The complexity of the factors controlling phosphorus loads in a given watershed is reflected in the inconsistencies observed in the sampling points falling outside the 95% confidence interval of the log–log regression models. The lack of any overarching patterns during times of increased flood or drought conditions (even with the consideration of antecedent weather conditions) indicates that the Altamaha Watershed is a highly buffered system. However, it is interesting to note that the instances in which DIP was lower than expected never occurred during the winter season, and of the 12 instances in which it was higher than expected, there was only one event during the winter. With regard to DOP, the instances in which concentrations were lower than expected never occurred during the summer season, and across the watershed, there were only four instances in which DOP was higher than expected, and these occurred only in the Altamaha and Ocmulgee rivers during the winter and the fall seasons.

Taken together, these results imply an interplay between DIP and DOP uptake in the Altamaha Watershed. The resuspension and settling of overlying clays in the Piedmont Province and the kaolin deposits in the Coastal Plain Province (Georgia EPD 1998, 2004*a*, *b*) are physical mediums that likely sorb organic and inorganic P (House 2003). Some biotic controls on DOP and DIP are uptake by algal mats and biofilms (Correll 1998, Withers and Jarvie 2008, Darch et al. 2014). As a result, the longer residence time of water across the sediment–water interface during summer times of low flow and high biological activity likely encourage both physical and biological uptake of DIP. As DOP bioavailability is seasonal and tends to increase during the winter (Monbet et al. 2008), it is possible that DOP is more readily taken up at this time as opposed to during the summer season.

Whole-watershed P-implications

The impacts of a steady increase in population density within the Altamaha Watershed are further reflected in the steady increase in septic tank installments and existing leaky systems in each subwatershed (U.S. Department of Commerce, 1969, 2000, and 2010 Censuses of Population and Housing, Georgia EPD 2012*a*, *b*, *c*). Evaluative reports assessing the fecal coliform loads in the Altamaha, Oconee, and Ocmulgee river basins indicate that from 2004 to 2009, the number of septic take installments in each subwatershed has substantially increased (Georgia EPD 2012*a*, *b*, *c*). This implies that P delivery will likely increase as a result. The inconsistencies in the timing of DIP or DOP values higher or below expected levels make it difficult to predict the effect of increased drought or flood on the P-dynamics. However, given that sediment P-uptake can be two times that of algae (Withers and Jarvie 2008) and increased water residence times will increase the potential for mineral precipitation to fix P to the sediments, prolonged periods of decreased flow (due to drought or increased water use) will likely increase the amount of P retained (or temporarily stored) within the Altamaha Watershed. If extreme dry, low-flow events are followed by extreme wet, high-flow events in which P is "flushed out" of the system without reentering any biogeochemical pathways (Withers and Jarvie 2008), it is possible that intense pulses of downstream export of P to the coast will occur. The ecological effect of this potential mechanism requires further investigation.

It is also apparent that DOP is the dominant P-form in the Ocmulgee, Little Ocmulgee, and Ohoopee tributaries and in the Altamaha. Combined with increased anthropogenic outputs, these results imply that the likelihood of increased DOP export out of the Altamaha River Watershed into the coastal estuary is increasing and could have downstream ecological implications for eutrophication. However, more research is necessary to fully understand its ecological importance—especially if DOP from particulate matter is a P source for phytoplankton and bacterial utilization (Correll 1998, Darch et al. 2014). The analysis of particulate phosphorus distribution and dynamics also needs additional attention. The strong sorption of P to sediment particles (House 2003, Romeis and Jackson 2005, Withers and Jarvie 2008) indicates that the already high P-concentrations in the Altamaha River were likely underestimated. Thus, further clarification of both dissolved and particulate inorganic and organic exports to the coast is necessary to fully understand the P-dynamics in this system.

Carbon, silicate, and total suspended solids dynamics

Watershed DOC and DIC concentrations are driven by both biotic and abiotic processes. The abiotic factors are dependent on temperature, topography, precipitation, geology, and soil types (Hope et al. 1994, Johnson et al. 2006, Andrade et al. 2011). DOC export in particular is closely related to the organic carbon content of topsoil and is strongly driven by the hydrologic behavior of quick-flow pathways over watershed surfaces (Kawasaki et al. 2005, Johnson et al. 2006). In contrast, DIC export is dominated by the natural weathering of minerals, groundwater inputs, and soil degassing at the sediment–water interface (Hope et al. 1994, Cai et al. 2008, Andrade et al. 2011, Tian et al. 2015). From a biotic standpoint, DOC concentrations are dependent on what is exuded by micro-, macro- and megafauna, such as algae, phytoplankton, bacteria, zooplankton, and fish during primary and secondary production as well as that produced by biological decay of detrital material and POC (Schlesinger 1997, Correll et al. 2001, Berman and Bronk 2003), whereas DIC fluxes are largely the result of root and microbial respiration within a watershed (Johnson et al. 2006). Anthropogenic influences on increased DOC fluxes into watersheds have been attributed to coupled increases in cropland and livestock presence (Correll et al. 2001, Weston et al. 2009). Increased DIC fluxes however have been indirectly related to increased nitrogen inputs via runoff from fertilizers and sewage, which, in turn, chemically increases the rates of mineral weathering and microbial respiration. Natural weathering processes and rate can also be modified by agricultural-based water use which promotes the production of DIC such as that in the Yellow River Basin (Cai et al. 2008). It is further promoted by climate changes as shown in the Mississippi River Basin (Raymond et al. 2008, Tian et al. 2015).

The abiotic, biotic, and anthropogenic factors discussed above contribute to the carbon dynamics in the Altamaha Watershed. In this study, the inverse relationship between DIC and DOC and the distinct separation in C-dynamics depending on subwatershed (Fig. 11) indicate that (1) in this watershed, the DIC and DOC dynamics are strongly coupled, and (2) the mechanisms driving the overall C-dynamics are vastly different depending on the subwatershed of interest. The following discussion does not aim to explain these mechanisms in full, as this is beyond the scope of the study, but based on the collected evidence, it provides plausible explanations that tease apart the potential drivers of C-cycling.

In agreement with Hope et al. (1994), we observed strong positive relationships between DOC concentration and discharge, indicating that much of the DOC that is transported by the Altamaha River and its tributaries likely comes from allochthonous sources (Fig. 11). Compared with the world average DOC concentration (520 μM, as reported by Meybeck and Ragu 2012), the median DOC concentrations in the Altamaha (430 μM), Ocmulgee (457 μM), and Oconee (416 μM) are similar. The median DOC concentrations in the Little Ocmulgee (1114 μM) and the Ohoopee (1034 μM) are much higher than the global mean (Appendix S1: Table S4).

We observed contrasting patterns in the dissolved inorganic form of carbon in the watershed. Strong negative relationships were observed between DIC and discharge (Fig. 11b). While the median DIC concentrations in the Altamaha (600 μM), Ocmulgee (693 μM), and Oconee (553 μM) were similar to the average concentration found in temperate, large rivers (564 μM; Barnes and Raymond 2009), opposite to the pattern observed for DOC dynamics, the Little Ocmulgee (334 μM) and Ohoopee

(282 μM) river DIC concentrations were much lower (Appendix S1: Table S4). These results must be considered within the context that DIC concentrations are regionally specific. Cai et al. (2008) found a 10-fold difference between DIC concentrations in the Mississippi and Amazon rivers (2000 and 200 μM, respectively), and Meybeck and Ragu (2012) found average DIC concentrations in world rivers range from 33 to 18 018 μM.

The regional specificity of DIC concentrations is further demonstrated in the dominance of inorganic carbon within the Altamaha and the two largest tributaries (the Ocmulgee and Oconee). This result is both expected and surprising. Stets and Striegl (2012) indicated that inorganic carbon export exceeded organic carbon export in the conterminous United States as a result of its underlying geology. The exception to this trend was observed along the Southeastern Atlantic Seaboard, where the trend was the opposite. A comparison of DOC:DIC dynamics across sites in this study disagrees with this conclusion. The results from this study indicate that the Altamaha is not an exception; instead, the two minor tributaries flowing into it (the Ohoopee and the Little Ocmulgee) are exceptions (Fig. 11c).

The strong positive relationships between total suspended solids (TSS), DOC, and discharge, respectively, imply that TSS could be an important source of DOC into the watershed (Fig. 9). This is supported by the assumption that the major sources of DOC into the Altamaha River Watershed were topsoil and resuspended sediments as a result of increased discharge (Hope et al. 1994, Nixon et al. 1995). Statistically, the variation in DOC was only explained by TSS in the Altamaha, Ocmulgee, and Oconee tributaries. The Ohoopee did not only demonstrate no relationship between TSS and DOC, but also exhibited the lowest median TSS concentration (Fig. 9; 15 mg dry sed L^{-1}). Preliminary results from the Little Ocmulgee demonstrated a similar dynamic (median TSS concentration: 16 mg dry sed L^{-1}, data not shown). These dynamics, coupled with the conspicuously high DOC content in the Little Ocmulgee and Ohoopee tributaries, are explained by the established physical characteristics of these sites, which identify them as "blackwater" streams (Beck et al. 1974, Weston et al. 2003, Georgia EPD 2004*a*, *b*). This classification explains the contrasting patterns between these two sites compared to those observed in the Altamaha, Oconee, and Ocmulgee rivers (Fig. 11). In the Little Ocmulgee and Ohoopee, the lower discharge and gently sloping geology has led to an internal accumulation of organic carbon (largely in the form of tannins and organic matter decomposition intermediates).

Although the results were not statistically significant, TSS export demonstrated a strong positive relationship with population density and livestock biomass (Figs. 4g and 6g). Coupled with the evidence that DOC concentrations are highly dependent on TSS, this suggests that DOC is indirectly impacted by anthropogenic influences in the Altamaha, Ocmulgee, and Oconee rivers. Furthermore, over a temporal scale, Weston et al. (2009) observed a positive relationship between agriculture and organic carbon export from this watershed; thus, it can be assumed that on a watershed scale, agriculture likely affects the DOC exports and concentrations.

Unlike DOC however, the main sources of DIC into the Altamaha Watershed are difficult to tease apart. The significant negative log–log relationships between both DIC and Si and discharge in the Altamaha and each of the tributaries, respectively, are indicative of dilution with an increase in water volume (Table 6). This strongly implies that the sources of DIC to the watershed are internal (i.e., from weathering and groundwater inputs) rather than from runoff and surface water exports. Further comparisons of the DIC concentrations in this watershed to other urban, forested, and agricultural streams suggest these sources are likely compounded by anthropogenic influences (Barnes and Raymond 2009). This is seen in the positive relationship observed between DIC export and population density (Fig. 4i).

The influence of weathering on DIC concentrations is also attributed to the underlying geology in the Upper Ocmulgee and Oconee subwatersheds. These regions lie in the Northern Piedmont Province, which is largely underlain by crystalline and metamorphic igneous rocks (Georgia EPD 1998). The combinations of weathering by surface water and recharge by groundwater during dry periods (a source shown to have a substantial contribution to stream DIC concentrations; Andrade et al. 2011) are likely strong contributors to the high DIC concentrations found just before their confluence with the Altamaha River. Urban influences aside, as the Altamaha River is ultimately a Piedmont River, we would predict the Ocmulgee and Oconee subwatersheds (and thus the Altamaha River Watershed as a whole) to have high DIC concentrations.

The Little Ocmulgee, Ohoopee, Lower Ocmulgee, Lower Oconee, and Altamaha subwatersheds are underlain by the Coastal Plain Province. These underlying sediments—sand and kaolin—are of marine origin (Georgia EPD 1998). The calcium carbonate base of marine-origin sediments would imply a significant amount of DIC input is likely within the lower reaches of the Altamaha Watershed. However, the significantly lower DIC concentrations observed in the Ohoopee and Little Ocmulgee tributaries indicate otherwise. This provides further evidence that the DIC sources into the Altamaha River Watershed are likely a combination of upper-watershed anthropogenic and weathering influences.

While silicate concentrations reflect weathering within a watershed, the magnitude of export is important downstream and to the coastal ocean. Similar to DIC, Si concentrations can be driven by physical changes in land use and urbanization. Carey and Fulweiler (2013) concluded that land use changes from a forested landscape to an urbanized one increased Si export from watersheds. This is a result of less Si uptake by terrestrial plants, which play a major role in the global Si cycle (Conley 2002). In contrast, the construction of dams and reservoirs encourages the settling and retention of particulate Si, making it less available for diatom use downstream (Humborg et al. 2000, Turner et al. 2003). Both of these factors likely impact the Altamaha River Watershed: Si distribution is likely hindered by the presence of Lake Sinclair, Lake Oconee, and Jackson Lake upstream and stimulated by increasing urbanization.

With the exception of the Ohoopee River (median Si, 92 μM), the median Si concentrations are above the world average of 150 μM (Appendix S1: Table S4; Carey and Fulweiler 2013). This indicates that despite the presence of notable dams in the Altamaha Watershed, either the Si concentrations have not been impacted by increased settling and retention of particulate Si, or there are significant Si inputs below the dams. The positive relationship observed between Si and population density documents the influence of urbanization on increased Si concentrations. It is likely that the presence of agriculture, urbanization, and natural weathering outweigh the potential removal of Si as a result of the constructed reservoirs. The increase in Si as a result of anthropogenic influences is not likely to offset the Si-limitation often found in coastal waters as N-exports have increased from anthropogenic influences as well (Carey and Fulweiler 2013). This is further supported by the median Si:DIN ratios which are well above the ideal, 1:1 ratio (Appendix S1: Table S4; Humborg et al. 2000). Preliminary assessment of the Si dynamics at the Altamaha River Mouth indicates the higher-than-average Si export continues into the coastal ecosystem downstream (Takagi et al. *in preparation*).

N, P, and C ratios

In the following discussion, it is important to note that the C-, N-, and P-concentrations throughout the Altamaha Watershed (N and P in particular) are well above the world averages for what are considered "pristine" rivers (Meybeck 1982, Dubrovsky et al. 2010). Up to this point, we have established that these dynamics are largely due to interactions between anthropogenic influences (population density, livestock biomass, and land use), hydrology, and underlying geology (especially with respect to P and DIC). We thus use the well-established N:P ratio of 16:1 to assess the relationship between N and P (both inorganic and organic forms) in the Altamaha Watershed and not solely as a measure of nutrient limitation for primary production. In line with the aim of this study, we are interested in better understanding the factors driving N:P and C:N ratios in the Altamaha Watershed.

When only the inorganic forms of N and P (DIN:DIP) are considered, a slightly different picture of the nutrient dynamics in the Altamaha River Watershed emerges than if both the inorganic and organic forms (TDN:TDP) are considered together. The median DIN:DIP ratios at each site were the closest to the Redfield ratio of 16:1 in the Oconee, Ohoopee, and Little Ocmulgee rivers. However, if the TDN:TDP ratios were considered, the Altamaha and Ocmulgee rivers moved closer to the 16:1 ratio, while the other three tributaries moved farther from it (Appendix S1: Table S3). This is attributed to the proportionately larger organic P than organic N fractions in the Altamaha and Ocmulgee rivers.

It is interesting to note that for the most part, neither the DIN:DIP nor the TDN:TDP ratios demonstrated a significant relationship with season or hydrology. This implies that the N:P dynamics across the watershed were well buffered regardless of precipitation, runoff, or groundwater inputs. Combined with the dominate presence of organic nitrogen and organic phosphorus, it became evident that (1) despite the anthropogenic influences in this watershed, nutrient processing is highly efficient, and (2) the organic N- and P-forms in this ecosystem must be biologically available. The bioavailability of organic N in the Altamaha Watershed is discussed by Wiegner et al. (2006). The significant increase observed in TDN:TDP ratio with discharge in the Ohoopee River is attributed to the products released during the breakdown of resuspended dissolved organic matter (DOM).

The presence of DOM (especially in the form of DOC) is prominent in the Ohoopee and Little Ocmulgee tributaries. As these two sites are considered "blackwater" rivers, they are expected to exhibit a higher amount of organic carbon. Here, the C-pool is likely largely comprised of recalcitrant organic matter in the form of humics (Alberts and Takacs 1999). However, unlike the N- and P-dynamics, the median DOC concentrations in the Altamaha, Ocmulgee, and Oconee rivers were close to the world averages (Meybeck 1982). These factors indicate that the biogeochemical cycling in the Ohoopee and Little Ocmulgee rivers vs. the Oconee, Ocmulgee, and Altamaha rivers is different. The C:N ratio can thus provide an indication of the quality of organic matter flowing through the Altamaha Watershed.

If we look at DOM quality with respect to DOC:DON, we observe that the median ratios are all under 25, except for the Ohoopee River which has a median ratio of 26 (Appendix S1: Table S4). This indicates that the DOM in these rivers is generally N-rich. If we look at DOC:TDN, the ratio is even lower, specifically with respect to the Ocmulgee River. Times when the DOM in these rivers is more N-limited is highly influenced by discharge. With the exception of the Little Ocmulgee, the log–log relationships between DOC:TDN, DOC:DIN, and DOC:DON and discharge were significantly positive across the watershed (Table 6). Thus, the balance of the C:N dynamics and the overall quality of organic matter transported throughout the Altamaha Watershed are hydrologically driven and location-dependent.

These results also indicate a third factor that could influence the carbon dynamics in a given watershed: fires. Over half of the instances in which the DOC:DON and DOC:TDN ratios were greater than expected across the watershed occurred during a period when there were two major fires in the Okefenokee Swamp (located approximately 97 km south–southwest of Doctortown, GA, the Altamaha River sampling site), from mid-April to late June in 2007 and in 2011. The increased DOM observed is attributed to burn-derived material imported into the watershed under high-wind conditions that brought restricted visibility as far north as Atlanta (~ 410 km northwest from the Okefenokee, part of the Upper Ocmulgee subwatershed). The second major fire in 2011 affected the DOC:DON ratio in the Altamaha River; however, further effects were not observed in the other tributaries. This was likely due to less severe wind conditions in 2011 compared to 2007.

Hydrology and climate

The overall discharge patterns of the Altamaha River and its main tributaries follow those observed by Davis et al. (2002). Stream flows are higher in the winter and spring and lower in the summer and fall. The average annual flow patterns (Appendix S1: Fig. S2) and flow-duration curves (Appendix S1: Fig. S3) clearly indicate that the discharge of the Altamaha River (1) is largely driven by the cumulative contribution of the four main tributaries (the Little Ocmulgee, Ocmulgee, Oconee, and Ohoopee rivers) and (2) is influenced by anthropogenic forcing.

The most obvious explanation for the decreased discharge observed in the rivers and tributaries of the Altamaha Watershed would be the construction of reservoirs and dams. However, if we consider changes in flow based on when the hydroelectric dams were constructed, we see that the implementation of dams is not solely responsible for this decrease. On the Ocmulgee River, the largest reservoir, Jackson Lake, was constructed in 1910 (Georgia EPD 2004*b*). On the Oconee River, Lake Sinclair began operation in 1953 and Lake Oconee began in 1979 (Georgia EPD 1998; Appendix S1: Fig. S2a–c). If a decrease in discharge were strictly due to dam construction, the Ocmulgee River should, in theory, have a similar average discharge pattern from 1932 to 2012 and the Oconee River discharge pattern should see an average overall decrease in the years following the opening of each dam. While the Oconee River does show a decrease in discharge from 1979 to 1999, after the opening of Lake Oconee (Appendix S1: Fig. S2b), the Ocmulgee and Altamaha rivers show a decrease as well (Appendix S1: Fig. S2a, c). This indicates that changes in overall discharge are likely driven by cumulative changes in population and water use and are exacerbated by changes in climate and the construction of hydroelectric dams. This is demonstrated in the dramatic drop in average discharge values from 2000 to 2012 observed in all three rivers. It is particularly evident in the Ocmulgee River which had the highest rate of population increase and the most shallow flow-duration curve (Table 3; Appendix S1: Fig. S3).

Further evidence of population-driven decreases in discharge is demonstrated in Appendix S1: Fig. S4. Here, the strong, negative log–log slope indicates discharge (specifically in the Altamaha) is well explained by increases in population density that occurred in the Ocmulgee and Oconee subwatersheds over the last 60 yr. While the gradual shift in rainfall (Appendix S1: Fig. S1) patterns may have also added to a decrease in discharge, our observations suggest that its effects have had a less dramatic effect than anthropogenic forcing.

When considering the influence of discharge, two geomorphological influences must be kept in mind. First, it should be noted that stepwise multiple linear regression of the average daily flow from 2000 to 2012 indicates that the tributary that best predicts the flow in the Altamaha River is the Ocmulgee River ($R^2 = 0.965$, df = 1, 364, $P < 0.001$). Yet if the same analysis is conducted on the sample-day flow values from 2000 to 2012, the tributary that best predicts the Altamaha River flow is instead the Oconee River ($R^2 = 0.985$, df = 1, 17, $P < 0.001$). Further analyses of both backward and stepwise multiple linear regression models indicate that the addition of either the Oconee or the Ocmulgee rivers to the models does not add more than 5% to the explanation of variance in the Altamaha River flow. This is logical as the land areas and subsequent volume of water drained by the Oconee and Ocmulgee River subwatersheds (Table 3) relative to the Ohoopee River subwatershed are similar.

Second, the average percent contribution (Appendix S1: Fig. S5b) indicates that the cumulative contribution of the tributaries to the overall flow of the Altamaha River (especially from September to December) can exceed 100%. This could imply a significant loss of water between the confluence of the Ohoopee River with the Altamaha and Doctortown. However, it is more likely that this decrease in flow is due to withdrawals by the nuclear power plant (Plant Hatch, located before the confluence with the Ohoopee River), decreases in river slope in the Coastal Plain, and an increase in floodplain area toward the coast. Furthermore, based on flow patterns alone, the flow of the Altamaha River will be dominated by waters brought in by the Ocmulgee River during low-flow periods, whereas during high-flow periods, the Ocmulgee and Oconee rivers have a more equal influence (Appendix S1: Fig. S5). This variation in cumulative discharge and the alternating influence of the Oconee and Ocmulgee tributaries on the Altamaha River flow (depending on flood condition and the time of year) highlight how watershed geomorphology is an important factor driving biogeochemical transport and dynamics in the Altamaha River system (Appendix S1: Figs. S5b, S6).

Conclusion

There is no doubt that humans have increased the global fluxes of nitrogen and phosphorus into aquatic ecosystems (Vörösmarty et al. 2000, Smith et al. 2003, Turner et al. 2003, Fitzpatrick et al. 2007, Schaefer and Alber 2007). It is also clear that riverine nutrient processes reduce the effects of increased terrestrial nutrient inputs (Mulholland 2004). However, the predominance of both organic nitrogen and phosphorus, correlations between population, livestock density, and the proportion of agricultural land with P- and N-dynamics, and the decrease in overall discharge as a result of increased populations found in this study underscore the need to (1) assess both the inorganic and organic nutrients exported into and out of watersheds and (2) integrate the effects of anthropogenic influences (on both nutrients and hydrology) and climate change when assessing the health of watershed ecosystems.

Specific to this system, the Oconee River is clearly the primary source of inorganic phosphorus, largely attributed to livestock excreta, while the Ocmulgee River is the primary source of dissolved inorganic nitrogen, largely attributed to urbanization and a higher population density in the upper subwatershed reaches. The high population density away from the coastline makes the Altamaha River Watershed a unique system. The distance between the primary sources of nutrient input and export to the coast allows for nutrient processing, settling, and uptake in the upper reaches of the watershed. The chemostatic observations of many of the parameters measured indicate that the Altamaha Watershed is well buffered and able to maintain a static concentration of some nutrients. This implies that any ecological effects on the watershed are a result of chronically high nutrient concentrations—a characteristic that should be carefully considered in further studies.

The strong correlations between population density and DIN exports as well as DIP exports and livestock biomass imply that the nutrient inputs into the Altamaha River Watershed will only continue to increase over time. These results must be considered in the context of increasing water demands (as a result of increased energy, domestic, and industrial use) and a changing climate—as are evident in the present and historical records of this study. Appendix S1: Fig. S4a is especially telling because it indicates that in the Ocmulgee and Oconee sub-basins, the population density has been steadily increasing over the last 60 yr. Furthermore, the log–log regression of discharge as a result of population density clearly indicates a decrease in discharge as a result of increasing population (Appendix S1: Fig. S4b). Additionally, climate predictions show little change in overall average precipitation. The prediction of more frequent "wetter" and "drier" events imply that the frequency and duration of low-flow and high-flow events will only increase.

This is particularly troublesome because Groffman et al. (2004) projected that the N-export in streams is more positively influenced by high-frequency, low-flow events in comparison with low-frequency, high-flow events. This is due to increased N-retention during drought and low-flow conditions (Kaushal et al. 2008) followed by short-lived pulses of nutrients that are "flushed" out of terrestrial systems. Subsequently, dilutions occur due to the increase in water volume during a high-flow event. Furthermore, previous models indicate that instream-based nitrogen removal efficiency decreases under high-discharge and high-loading conditions as compared to moderate/low-loading conditions (Inwood et al. 2007, Mulholland et al. 2008, Alexander et al. 2009). This is attributed to a decrease in DIN residence time due to increased flows and the limited capacity of the tributaries to mitigate pulses of increased DIN loads (Inwood et al. 2007, Mulholland et al. 2008). Each of these factors contributes to increased N-export with increased discharge. These increases could be compounded by lag times (up to years) in NO_3^- additions through groundwater recharge pathways (originating from agricultural sources; Tesoriero et al. 2013). N-concentrations thus need continued monitoring to ensure the stability of the Altamaha Watershed Ecosystem.

The DOC:TDN and DIN:DIP ratios during flood conditions in our results are the least favorable for eutrophication. However, if low-flow events become more frequent, as is implied by the historical decrease in average precipitation during spring and summer (Appendix S1: Figs. S1, S2), the low DIN:DIP and DOC:TDN ratios that are observed under drought conditions would be sustained over longer temporal scales, pushing the system toward eutrophic conditions both in stream and at the coast. This could further create a more autotrophic system, in which the amount, quality, and spatial distribution of river productivity could shift (Finlay 2011). Thus, it is apparent that the more N that is exported, the further away the C:N:P:Si ratios will be from the ratios most ideal for the growth/limitation of microbial and phytoplankton communities responsible for primary production and nutrient cycling (Redfield 1958). As it is, the C:N ratios in this study already indicate the DOM is N-rich. A limit or overabundance of any of these elements may have already drastically changed the microbial community and had rippling effects on the riverine and coastal structure. This warrants the need for further studies comparing the microbial community in more "pristine" watersheds and the Altamaha Watershed.

The results of this study clearly demonstrate that the effects of anthropogenic forcing (i.e., agriculture, livestock, sewage, industry) easily outweigh those of climate as agents of change within the Altamaha River Watershed. Here, we provide a baseline for understanding the interactions between these two agents on both water quality and quantity. Further studies need to monitor and consider all aspects of a watershed—from biotic and abiotic interactions to inorganic/organic nutrient dynamics, climate patterns, water sources, and supply to effectively maintain our water resources and aquatic ecosystems.

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Supporting Information

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