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RESEARCH ARTICLE

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The influence of the coastal plain on the downstream material fluxes from a small coastal mountainous river basin

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Abstract

Small mountainous coastal basins display steeper gradients, suggesting intensified river transport. However, there is little information about downstream trends in rivers with low discharge and material fluxes across coastal plains and its influence on land-sea material transport. This study examined 2 years of river discharge, suspended sediment and nutrient concentrations, fluxes and yields from upstream to the upper estuary of a typical South-east Atlantic Basin. This study provides data about the material retention capacity of the coastal plain. The results indicated that the coastal plain did not affect nutrient concentrations, but reduced turbidity, inducing chlorophyll *a* and consequently primary productivity in the lower river basin and upper estuary. The coastal plain attenuated the increasing downstream material fluxes, but also curbed suspended sediment and TN fluxes, across the lower river/upper estuary. In contrast, TP and PO_4^{3-} fluxes increased sharply across the coastal plain. This was influenced by natural and anthropogenic P inputs from soils and run-off to the river channel. These exceeded the retention capacity of the coastal plain and result in a high export efficiency of this nutrient to the sea.

KEYWORDS
Atlantic Forest, mountainous coastal river, nutrient fluxes, small basin, water quality

1 | INTRODUCTION

Although small coastal river drains less than 20% of the continental land, they have a significant global material fluxes to the ocean (Milliman & Syvitski, 1992). Such watersheds also make an important contribution to the global carbon cycle, as they deliver large amounts of dissolved organic carbon to the coast that may be retained within estuaries, reducing export to the adjacent coast (Goldsmith et al., 2015; Lyons, Nezat, Carey, & Hicks, 2002; Moyer, Powell, Gordon, Long, & Bliss, 2015). In general, basin area and maximum altitude are primary factors controlling sediment delivery, with climate and run-off appearing to be secondary factors. (Milliman & Farnsworth, 2011; Milliman & Meade, 1983; Milliman & Syvitski, 1992). For nutrients, basin fluxes appear to be related to rainfall, although geomorphology, soil type, land use and human activities also control the concentrations and fluxes (Andrade et al., 2011; Dassenakis et al., 1998; Goldsmith et al., 2015; Moyer et al., 2015; Nicolau, Lucas, Merdy, & Raynaud, 2012).

The efficient transportation reported for small mountainous coastal basins has been attributed to their steep slope. This is a key parameter controlling velocity, water discharge and material transport, suggesting a seaward intensification of river discharge (Cohen, Wan, Islam, & Syvitski, 2018; Milliman & Syvitski, 1992). However, land–sea material transport from small mountainous coastal rivers may be different to that of large rivers, because such large watersheds usually have extensive floodplains, deltas and estuaries that retain and store material during the seaward transport (Nyberg, Gawthorpe, & Helland-Hansen, 2018). Small rivers draining to the ocean typically have small floodplains, deltas and estuaries, which, when associated with the high slope and episodic climate-driven dynamics, results in the discharge of materials as a hyperpycnal discharge (Mertes & Warrick, 2001) rather than the hypopycnal plumes, as described for larger drainage basins (Mulder & Syvitski, 1995).

Even within narrow coastal plains, it is important to determine if material fluxes from small rivers to the ocean are subject to retention within such areas, as exemplified by medium/large rivers where sediment fluxes are reduced due to the reduced erosion and deposition across the alluvial coastal plain (Slaterry & Phillips, Slattery & Phillips, 2011). Nutrient retention within coastal plains varies among rivers, but those that efficiently export nutrients seaward usually receive higher nutrient loads from the surrounding catchment, although there are limited data for small coastal rivers (Tysmans, Löhr, Kroeze, Ivens, & van Wijnen, 2013). In addition, all rivers experience reduced water velocities and increased water residence times with coastal plain areas. When discharge reaches the upper estuary, particle deposition and changes in water quality and chemical speciation occur (Tappin, 2002). Exceptions may occur during episodic high-discharge events, when rivers force the tide back and discharge directly into the coastal ocean with little influence of the coastal plain or estuary (Mertes & Warrick, 2001; Milliman & Farnsworth, 2011). Thus, our study hypothesized that small mountainous coastal rivers are efficient in delivering materials to the coast, due to the high/moderate slope across small basin length. However, they would be less important in terms of sediment and nutrient retention compared to medium and large watersheds due to the reduced size of the coastal plain and estuary. This study determined the whole-basin seasonal discharge, suspended sediment and nutrient concentrations, fluxes and yields of a small mountainous coastal watershed to investigate the influence of the coastal plain on seaward material transport.

2 | MATERIAL AND METHODS

2.1 | Study area

The Brazilian coast can be divided into the Northern Quaternary, Eastern Tertiary (Barreiras Formation), South-eastern Granitic and Southern Quaternary areas. From 22°S to 29°S, the transition between the tertiary and granitic coast is characterized by a mountain chain (Serra do Mar), with elevations higher than 1,000 m, parallel and near to the coast, forming a series of small drainage basins ($<10^{-1}$ to 10^4 km^2), termed as South-east Atlantic Basins (Knoppers, Ekau, & Figueiredo, 1999). Over several centuries, extensive human occupation of these coastal basins has occurred and account for about 60% of the Brazilian population. This has profoundly modified land cover, with only 15% of the local Atlantic Rainforest remaining (Ribeiro, Metzger, Martensen, Ponzoni, & Hirota, 2009).

The Macaé River basin, with an area of 1,765 km^2 and length of 136 km, is an example of a South-east Atlantic Basin (Figure 1). Topography, land use and anthropogenic changes to stream geomorphology, such as the removal of river meanders, suggest an intensification of fluvial transport into the coast (Marçal, Brierley, & Lima, 2017). The main channel is supplied by 20 smaller rivers, with Sana River and São Pedro River as important tributaries. Molisani et al. (2019) estimated that 46.9% of the basin was covered by Atlantic Forest, 46% by animal livestock and agriculture areas, 2.4% by urbanization and 4.7% by other land uses.

2.2 | Sampling and methodology

From February 2012 to February 2014, river discharge, suspended sediment and total and dissolved nutrients (C, N, P and Si) were determined from the upper stream (HW), in the transitional upper/middle river (Up/Mi), middle river (Mi) and lower river/upper estuary (Low/Up), and two tributaries—Sana (ST) and São Pedro (SPT). The sampling sites covered the whole basin topography, from upstream (HW, Up/Mi) to the coastal plain area through to the upper estuary (Mi, Low/Up) (Figure 1). Monthly sampling allowed measurement spanning rainy and dry periods and transportation events, including episodic flood-driven events, to determine the seasonal effects of the coastal plain on fluxes.

Water discharge (Q, m^3 s^{-1}) was obtained by measuring transversal river cross-section areas (depth and width) and current velocities using a manual current metre (General Oceanic). Water samples were collected using high-density PET bottles (upstream sites) and a Van Dorn bottle (lower river/upper estuary) and stored in clean flasks (1.0 N HCl pre-washed) and returned in an icebox to the laboratory. Due to the low river depth at most sampling sites for most sampling events, current measurements and water sample were collected in the middle of the channel, ~0.3 m below the surface. In the lower river/upper estuarine section, samples were collected from both the middle and marginal channel, as well as at the surface (~0.3 m) and at ~1.0 m above the riverbed. During the sampling events, the coefficient of variation among replicates from the river cross-section varied from 4.2 to 19% for nutrients and suspended sediment. Dissolved oxygen, pH, temperature, conductivity and salinity were measured in situ using a multi-parameter probe (YSI 556). In the laboratory, the samples were filtered, in duplicate, through cellulose acetate membranes (0.45 μm pore diameter) for the gravimetric analysis of suspended sediment (SS) concentrations. The filtered samples were used for the dissolved nutrient analysis, while unfiltered samples were used for total nutrient determinations. Samples were also filtered through fiberglass membranes for chlorophyll *a* analyses. Water samples were analysed by spectrophotometric methods for ammonium (NH_4^+ indophenol blue method), orthophosphate (PO_4^{3-} ascorbic acid molybdate method) and dissolved silica (D-Si) (ammonium molybdate method). Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured by high-temperature catalytic oxidation (Shimadzu TOC- 5000). Non-filtered samples were simultaneously digested for total nitrogen (TN) and total phosphorous (TP) (persulphate method) determination (APHA, 2005). Chlorophyll *a* determination was carried out by 90% acetone extraction and spectrophotometric analysis (APHA, 2005). All analyses were performed in duplicate (precisions

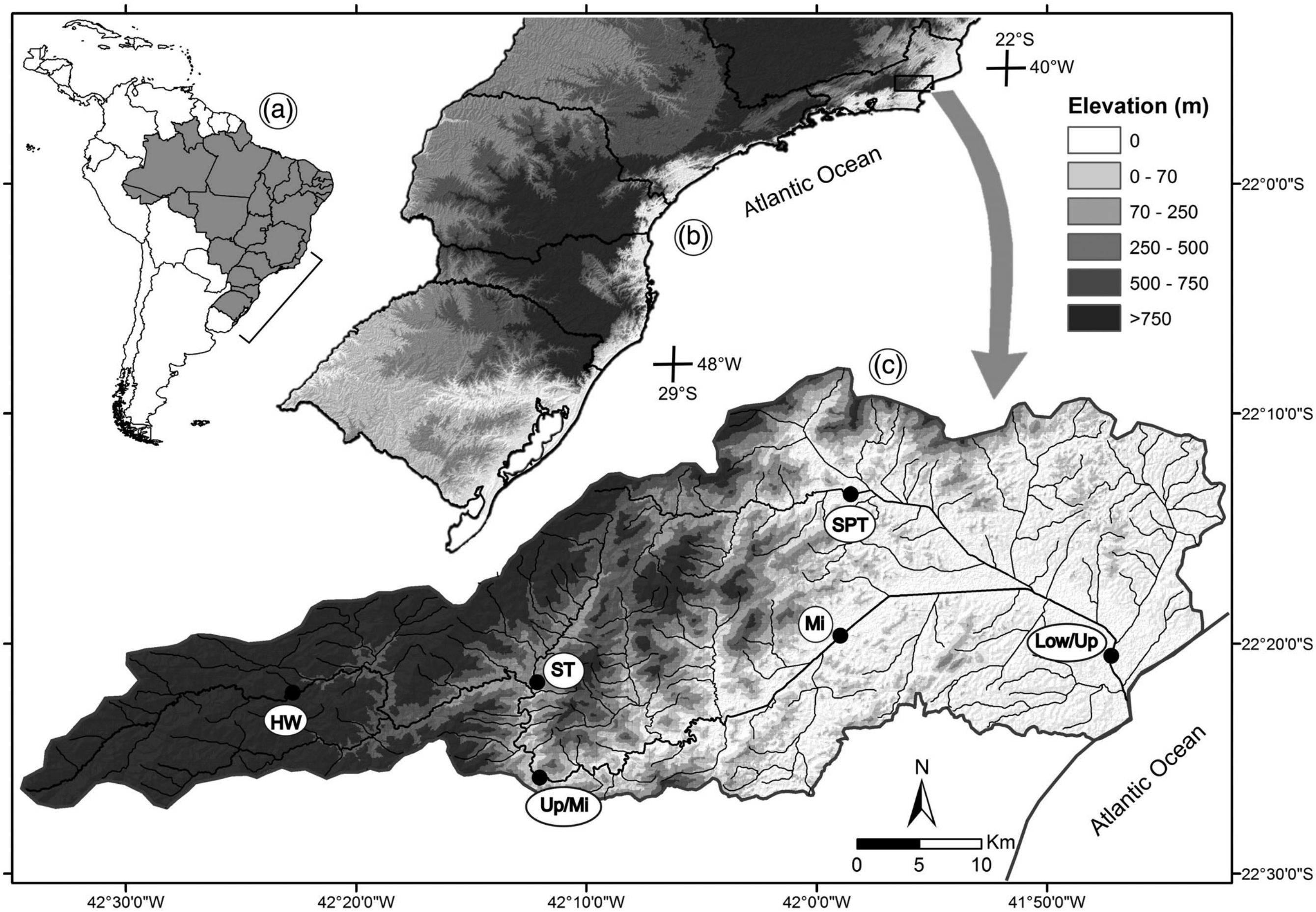

FIGURE 1 Map of the study area and sampling sites across the upper (HW), upper/middle (Up/Mi), middle (Mi), lower river/upper estuary (Low/Up) and Sana/São Pedro tributaries (ST and SPT) on the Macaé River basin

between replicates for all nutrients were about 10%) using analytical blanks.

The instantaneous fluxes of suspended sediment and nutrients were calculated by multiplying the concentrations by the river discharge. The annual loads were estimated using the average instantaneous load method presented in Equation (1) (Preston, Bierman, & Silliman, 1989):

$$F = k\sum_{i=1}^{n}\frac{CiQi}{n}, \tag{1}$$

where F is the annual load (t year^{-1}), Ci is the concentration of suspended sediment and nutrients (mg L^{-1}), Q_i is the concomitant instantaneous discharge (m^3 s^{-1}), n is the number of days presenting concentration and discharge data and K is the conversion factor used for the annual period. For the seasonal analysis, the same calculation was performed, but K grouped data from both the dry (April to October) and rainy (November to March) months, following the long-term rainfall for the studied watershed. Suspended sediment and nutrient yields were also calculated by dividing the annual fluxes by the upstream area of each sampling site, measured by remote sensing.

The D'Agostino–Pearson omnibus normality test was used to verify if the data displayed a Gaussian distribution. If the data displayed a normal distribution, a one-way analysis of variance (ANOVA) followed by Dunnett's test (parametric) was undertaken; if not normal, a Kruskal–Wallis test followed by Dunn's test (nonparametric) was employed to test for statistically significant differences among river sections and seasons. A correlation matrix was used to determine data inter-correlations. Differences at the 0.05 level were reported as significant.

3 | RESULTS

On average, DOC, TN, TDN and TP concentrations were not statistically different across the river basin ($p > .05$), while PO_4^{3-} and NH_4^+ concentrations were higher only on the Sana and São Pedro tributaries, respectively (Table 1, Figures 2 and 3). Chlorophyll concentrations were higher in the lower river/upper estuary, which also had the lowest suspended sediment concentrations ($p < .05$), due to the decreased water velocity from the upper basin (0.74 m s^{-1}) to the estuary (0.24 m s^{-1}). Thus, at the head of the estuary, chlorophyll

TABLE 1 Mean (*SD*) of physical–chemical parameters measured across the Macaé River channel and tributaries (Sana e São Pedro)

	Upper	Upper/Middle	Middle	Lower river/Upper estuary	Sana	S. Pedro
Discharge ($m^3 s^{-1}$)	3.3 ± 1.7	14 ± 13	32 ± 31	34 ± 32	3.1 ± 2.5	10 ± 11
Velocity ($m s^{-1}$)	0.70 ± 0.2	0.45 ± 0.2	0.71 ± 0.2	0.24 ± 0.2	0.44 ± 0.1	0.74 ± 0.2
pH	6.5 ± 0.8	6.7 ± 0.7	6.6 ± 0.6	6.9 ± 0.7	6.7 ± 0.7	6.8 ± 0.5
Cond. ($\mu S cm^{-1}$)	26 ± 17	37 ± 30	43 ± 42	55 ± 49	36 ± 23	39 ± 32
DO (%)	102 ± 15	99 ± 13	87 ± 15	81 ± 13	102 ± 14	94 ± 9.0
SS ($mg L^{-1}$)	2.9 ± 3.0	17 ± 19	28 ± 23	5.1 ± 5.7	7.7 ± 16	26 ± 41
Chl-*a* ($\mu g L^{-1}$)	1.2 ± 0.7	3.8 ± 6.6	2.7 ± 2.0	4.6 ± 3.8	1.4 ± 1.1	3.0 ± 2.2
DOC ($mg L^{-1}$)	2.1 ± 1.5	1.8 ± 16	2.1 ± 1.3	2.1 ± 1.4	2.8 ± 2.3	3.0 ± 2.0
TN ($\mu g L^{-1}$)	587 ± 579	508 ± 352	617 ± 907	598 ± 750	586 ± 471	671 ± 583
TDN ($\mu g L^{-1}$)	366 ± 144	318 ± 128	335 ± 121	369 ± 130	387 ± 144	436 ± 158
NH_4^+ ($\mu g L^{-1}$)	41 ± 35	32 ± 44	28 ± 26	35 ± 27	45 ± 40	72 ± 82
TP ($\mu g L^{-1}$)	84 ± 120	79 ± 111	71 ± 112	132 ± 138	129 ± 128	123 ± 09
PO_4^{3-} ($\mu g L^{-1}$)	15 ± 7.0	27 ± 23	18 ± 16	28 ± 22	49 ± 69	22 ± 16
D-Si ($mg L^{-1}$)	11 ± 2.4	17 ± 4.2	14 ± 5.2	15 ± 4.0	13 ± 3.2	13 ± 3.3

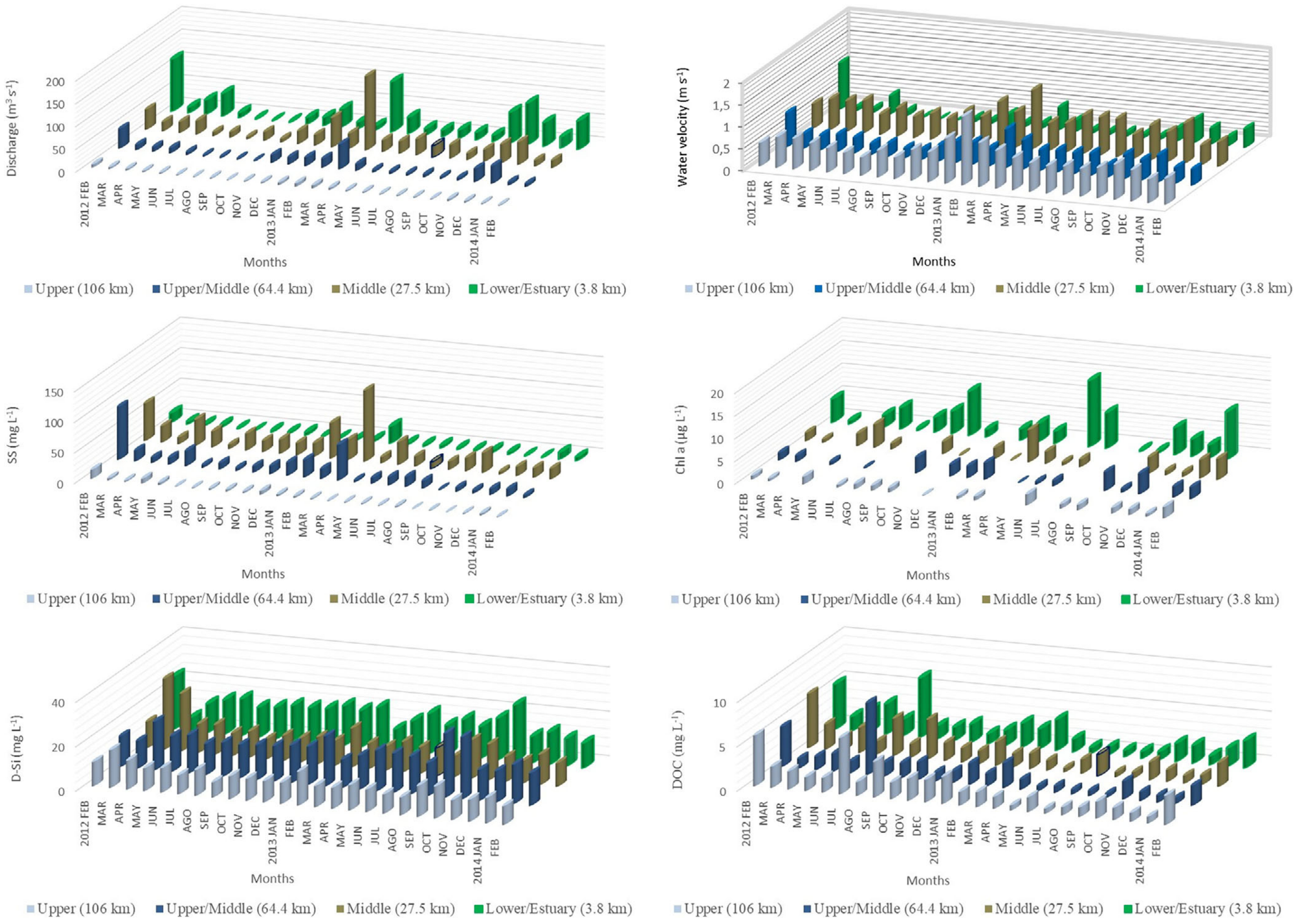

FIGURE 2 Spatial and temporal variation of water discharge ($m^3 s^{-1}$), velocity ($m s^{-1}$), suspended sediment, dissolved organic carbon and dissolved silica ($mg L^{-1}$) and chlorophyll *a* concentrations ($\mu g L^{-1}$) in the main channel of the Macaé River [Colour figure can be viewed at wileyonlinelibrary.com]

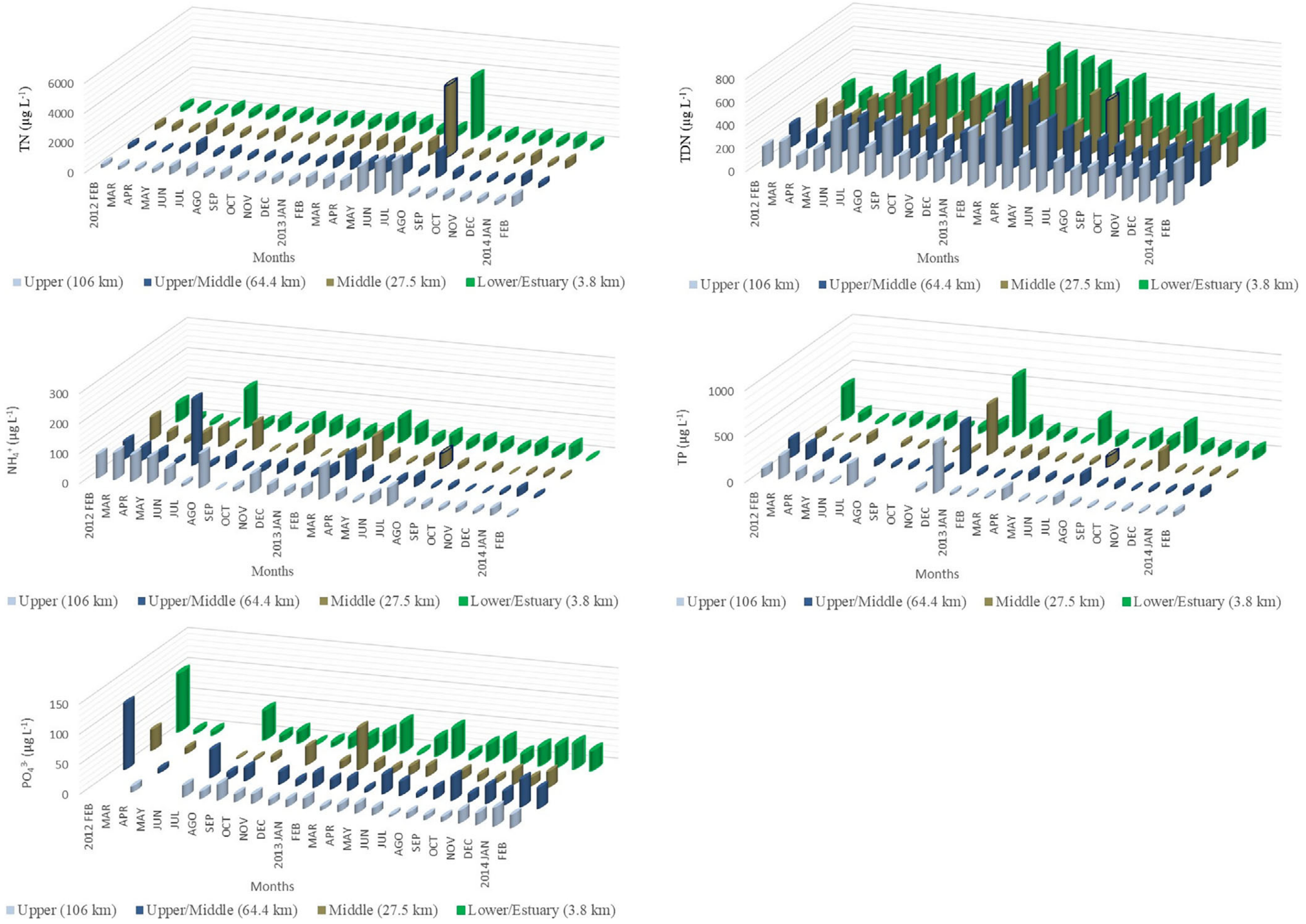

FIGURE 3 Spatial and temporal variation of total phosphorous (TP), total nitrogen (TN), total dissolved nitrogen, ammonium and orthophosphate concentrations (µg L^{-1}) in the main channel of the Macaé River [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Significant correlations (*p* < .05) among variables in the main channel and tributaries of the Macaé River basin

Upper	Upper/Middle	Middle	Lower river/Upper estuary	Sana	S. Pedro
DOC × SS $r^2 = 0.43$ *p* = .03	Q × SS $r^2 = 0.70$ *p* = .001	Q × SS $r^2 = 0.82$ *p* = .01	Q × SS $r^2 = 0.62$ *p* = .001	SS × DOC $r^2 = 0.89$ *p* = .04	SS × TDN $r^2 = 0.48$ *p* = .01
$NH_4^+ \times PO_4^{3-}$ $r^2 = -0.44$ *p* = .04	SS × PO_4^{3-} $r^2 = 0.62$ *p* = .003	SS × NH_4^+ $r^2 = 0.54$ *p* = .04	SS × PO_4^{3-} $R^2 = 0.52$ *p* = .01	$NH_4^+ \times PO_4^{3-}$ $r^2 = 0.62$ *p* = .02	TN × TDN $r^2 = 0.51$ *p* = .04
TN × TDN $r^2 = 0.42$ *p* = .04	TN × TDN $r^2 = 0.49$ *p* = .01	TN × TDN $r^2 = 0.43$ *p* = .03	DOC × PO_4^{3-} $r^2 = 0.53$ *p* = .008	Q × NH_4^+ $r^2 = 0.60$ *p* = .01	Q × TDN $r^2 = 0.42$ *p* = .03
Chl *a* × TP $r^2 = -0.55$ *p* = .03	DOC × PO_4^{3-} $r^2 = 0.48$ *p* = .02	Q × TDN $r^2 = 0.48$ *p* = .03	TP × D-Si $r^2 = 0.50$ *p* = .01	Q × SS $r^2 = 0.077$ *p* = .001	Q × PO_4^{3-} $r^2 = 0.48$ *p* = .03
Chl *a* × TN $r^2 = 0.58$ *p* = .01				Q × PO_4^{3-} $r^2 = 0.68$ *p* = .005	Q × SS $r^2 = 0.75$ *p* = .001
				Q × DOC $r^2 = 0.54$ *p* = .005	TP × PO_4^{3-} $r^2 = 0.47$ *p* = .04
				SS × TP $r^2 = 0.41$ *p* = .004	
				SS × NH_4^+ $r^2 = 0.67$ *p* = .001	
				SS × PO_4^{3-} $r^2 = 0.89$ *p* = .001	

TABLE 3 Instantaneous, seasonal (g s^{-1}) and biannual fluxes (t y^{-1}) and yields (t km^{-2} y^{-1}) of river discharge, nutrients and suspended sediment across the main channel and tributaries (Sana and São Pedro) of the Macaé River basin

	Upper	Upper/Middle	Middle	Lower river/Upper estuary	Sana	S. Pedro
Discharge						
Mean	3.3	14	32	34	3.1	10
rainy/dry (m^3 s^{-1})	4.4/2.5	24/6.4	45/21	50/21	3.8/2.5	15/6.6
2012–2013 (m^3 s^{-1})	3.2 ± 1.7	12 ± 11	24 ± 17	26 ± 32	3.1 ± 3.0	5.7 ± 4.7
2013–2014 (m^3 s^{-1})	3.5 ± 1.7	16 ± 16	38 ± 39	41 ± 33	3.0 ± 2.1	15 ± 13
Yield (hm^3 km^2 y^{-1})	1.1	4.1	1.2	7.6	0.11	0.19
Suspended sediment						
Mean	11	406	1437	282	53	587
rainy/dry (g s^{-1})	19/6.0	842/63	2697/447	541/79	109/9.0	1223/87
2012–2013 (t y^{-1})	549 ± 844	14362 ± 32156	27725 ± 36138	6274 ± 15,703	2884 ± 8,537	6576 ± 15,882
2013–2014 (t y^{-1})	176 ± 168	10953 ± 26694	60073 ± 15880	11044 ± 25484	483 ± 869	28938 ± 86448
Yield (t km^{-2} y^{-1})	4.0	117	85	63	2.0	11
DOC						
Mean	7.0	28	65	88	11	36
rainy/dry (g s^{-1})	11/4.5	51/10	98/40	148/41	18/6.2	63/15
2012–2013 (t y^{-1})	315 ± 314	1,000 ± 1,648	2,296 ± 2,382	2,735 ± 5,055	483 ± 729	829 ± 1,268
2013–2014 (t y^{-1})	147 ± 101	744 ± 1,254	1759 ± 2,192	2,730 ± 3,450	236 ± 402	1,388 ± 2,116
Yield (t km^{-2} y^{-1})	2.5	8.0	3.8	19	0.41	0.68
TN						
Mean	2.0	7.0	20	18	2.0	8.0
rainy/dry (g s^{-1})	1.9/2.0	10/3.7	24/18	24/14	2.2/1.6	12/4.6
2012–2013 (t y^{-1})	32 ± 16	116 ± 98	301 ± 239	288 ± 327	46 ± 53	78 ± 87
2013–2014 (t y^{-1})	84 ± 66	292 ± 348	928 ± 1,222	827 ± 855	71 ± 72	408 ± 625
Yield (t km^{-2} y^{-1})	0.64	1.9	1.2	4.1	0.07	0.15
TDN						
Mean	1.0	5.0	12	12	1.0	5.0
rainy/dry (g s^{-1})	1.4/0.80	8.6/2.1	18/7.1	18/7.2	1.5/0.9	7.8/2.7
2012–2013 (t y^{-1})	24 ± 11	81 ± 71	192 ± 121	187 ± 216	25 ± 18	56 ± 53
2013–2014 (t y^{-1})	42 ± 35	220 ± 317	523 ± 785	535 ± 551	46 ± 57	242 ± 312
Yield (t km^{-2} y^{-1})	0.36	1.4	0.69	2.7	0.04	0.09
NH_4^+						
Mean	0.15	0.55	1.1	1.3	0.20	0.78
rainy/dry (g s^{-1})	0.2/0.11	0.9/0.24	1.9/0.50	2.2/0.60	0.3/0.12	1.1/0.51
2012–2013 (t y^{-1})	5.7 ± 5.1	17 ± 23	23 ± 29	32 ± 60	8.4 ± 18	19 ± 31
2013–2014 (t y^{-1})	3.7 ± 5.6	17 ± 39	46 ± 112	48 ± 74	4.0 ± 6.3	29 ± 43
Yield (t km^{-2} y^{-1})	0.051	0.16	0.067	0.29	0.007	0.015
TP						
Mean	0.26	1.2	2.2	5.5	0.44	1.2
rainy/dry (g s^{-1})	0.39/0.15	24/0.34	3.5/1.3	9.3/2.6	0.77/0.19	1.9/0.61
2012–2013 (t y^{-1})	12 ± 16	59 ± 102	64 ± 112	202 ± 409	20 ± 34	23 ± 30
2013–2014 (t y^{-1})	4.1 ± 5.0	19 ± 14	73 ± 102	142 ± 166	7.6 ± 5.2	49 ± 41
Yield (t km^{-2} y^{-1})	0.087	0.35	0.13	1.2	0.016	0.022
PO_4^{3-}						
Mean	0.040	0.43	0.50	1.2	0.23	0.25
rainy/dry (g s^{-1})	0.054/0.026	0.87/0.086	0.92/0.18	2.4/0.29	0.48/0.035	0.41/0.12
2012–2013 (t y^{-1})	1.2 ± 0.8	13 ± 42	16 ± 16	37 ± 99	7.1 ± 32	7.7 ± 11
2013–2014 (t y^{-1})	1.6 ± 1.0	11 ± 11	21 ± 25	41 ± 47	2.9 ± 3.2	14 ± 17
Yield (t km^{-2} y^{-1})	0.013	0.12	0.030	0.27	0.008	0.005

TABLE 3 (Continued)

	Upper	Upper/Middle	Middle	Lower river/Upper estuary	Sana	S. Pedro
D-Si						
Mean rainy/dry (g s^{-1})	37 50/27	225 362/117	412 578/283	535 746/371	39 47/33	133 173/103
2012–2013 (t y^{-1})	1085 ± 676	6035 ± 5,100	10685 ± 7,446	14867 ± 23,499	1259 ± 1,369	2153 ± 1837
2013–2014 (t y^{-1})	1187 ± 772	7847 ± 6387	14737 ± 13743	18221 ± 14585	1164 ± 634	5974 ± 4246
Yield (t km^{-2} y^{-1})	12	65	24	120	1.4	2.5

a increased by 180%, while suspended sediment decreased by 560% compared to the middle river. At the basin scale, comparing TN and TDN concentrations, the chemical speciation analyses indicated that most nitrogen was in its dissolved form, with no statistically significant spatial variation. For phosphorous, speciation analyses indicated that, on average, PO_4^{3-} represented 38% of TP, and thus most of this nutrient was present in its particulate form.

The correlations among river basin parameters are presented in Table 2. Variable strengths of correlations suggest different fluvial processes acting in different river sections. The middle and lower river/upper estuaries across the coastal plain displayed similar correlations between discharge and suspended sediment concentrations. Although channel morphology differed from upstream towards the downstream coastal plain sites, many correlations and, consequently, in-stream processes were similar among areas. Correlations among nutrients suggest a similar emission source, while positive correlations among nitrogen, phosphorous, river discharge and suspended sediment suggest that river discharge exerts a strong control on nutrient and suspended sediment concentrations.

Considering the whole-basin, the rainy season coincided with higher river discharge, suspended sediment and TP and phosphate concentrations ($p < .05$). In contrast, only TN was present at higher concentrations during the dry season. Chlorophyll *a*, dissolved organic carbon, total dissolved nitrogen, ammonium and silica concentrations were similar between seasons. Episodic concentration peaks for most parameters were observed in both the rainy and dry seasons, with higher peak concentrations observed in both upstream river and across downstream coastal sites. Seasonal differences of nutrient concentrations between the rainy and dry seasons were not observed among upstream and coastal plain sites. Chlorophyll *a* did not display any clear spatial pattern during the rainy season. In the dry season, the lower river/upper estuary contained 284% more chlorophyll than the upper river, and across the coastal plain sites (from Mi to Low/Up) Chl-*a* increased by 92%. For river discharge during the rainy season, only the upper river differed (lower) to the middle and lower/upper estuaries. Statistically, during the dry season, both the middle and lower reaches had similar river discharge. For suspended sediment, during the rainy season, a 750% increase was observed from the upper to the middle reaches, and a 385% reduction across the coastal plain sites (Mi and Lo/Up). During the dry season, suspended sediment concentrations increased from the upper to middle river (904%) and then decreased 550% in the lower/upper estuary. Inter-annual measurements indicated similar suspended sediment and phosphate concentrations, and higher DOC, NH_4^+ and TP concentrations in 2012–2013 and of TN, TDN and D-Si in 2013–2014.

Table 3 and Figure 4 display river discharge, suspended sediment and nutrient fluxes across the basin. In general, mean instantaneous fluxes increased downstream. Fluxes of D-Si, DOC, TDN and NH_4^+ were intensified from the upstream to the middle river, but rates levelled off, or were reduced across the coastal plain (Mi and Low/Up). For example, total dissolved nitrogen fluxes increased 366% from the upstream sites to the middle basin, but at the basin's mouth fluxes increased by only 1% between the middle and lower basin/upper estuary. TP and PO_4^{3-} fluxes also increased downstream, but the fluxes increased markedly from the middle to the lower basin (147 and 131%, respectively). In contrast, suspended sediment and TN steadily increased downstream, but the fluxes reduced from the middle river to the lower basin/upper estuary. Suspended sediment increased by 3,448% from the upper to upper/middle river, 253% from the upper/middle to middle river and then fluxes reduced by 408% within the lower river/upper estuary. For TN, fluxes increased from the upstream to middle river (250 and 202%, respectively), and then reduced in the upper estuary (26%). When analysing the material fluxes during the dry and rainy seasons, the coastal plain always experienced a reduction on fluxes, primarily during the dry seasons. However, there were still periods of episodic high material fluxes, as measured in March 2013, when the lower river basin and upper estuary also retained suspended sediment, TN, TDN, TP and D-Si, but experience increased seaward export of river discharge, DOC, NH_4^+ and PO_4^{3-}, although at lower rates than in reported for the upstream sites.

Among tributary contributions, the Sana River contributed between 13 and 54% of the material fluxes passing through the upper and upper/middle river sections, with the highest contribution for PO_4^{3-} and the lowest for suspended sediment. The São Pedro River provided inputs to the lower river/upper estuary section corresponding 21–58% of the fluxes; being highest for NH_4^+ and lowest for TP (Figure 4). Thus, tributaries can contribute significantly to the material fluxes, both in the mountainous and coastal plain portion of this small coastal catchment. Typically, fluxes were higher during the rainy season, except for TN at the Sana tributary, which were similar between seasons. Intra-annual fluxes were

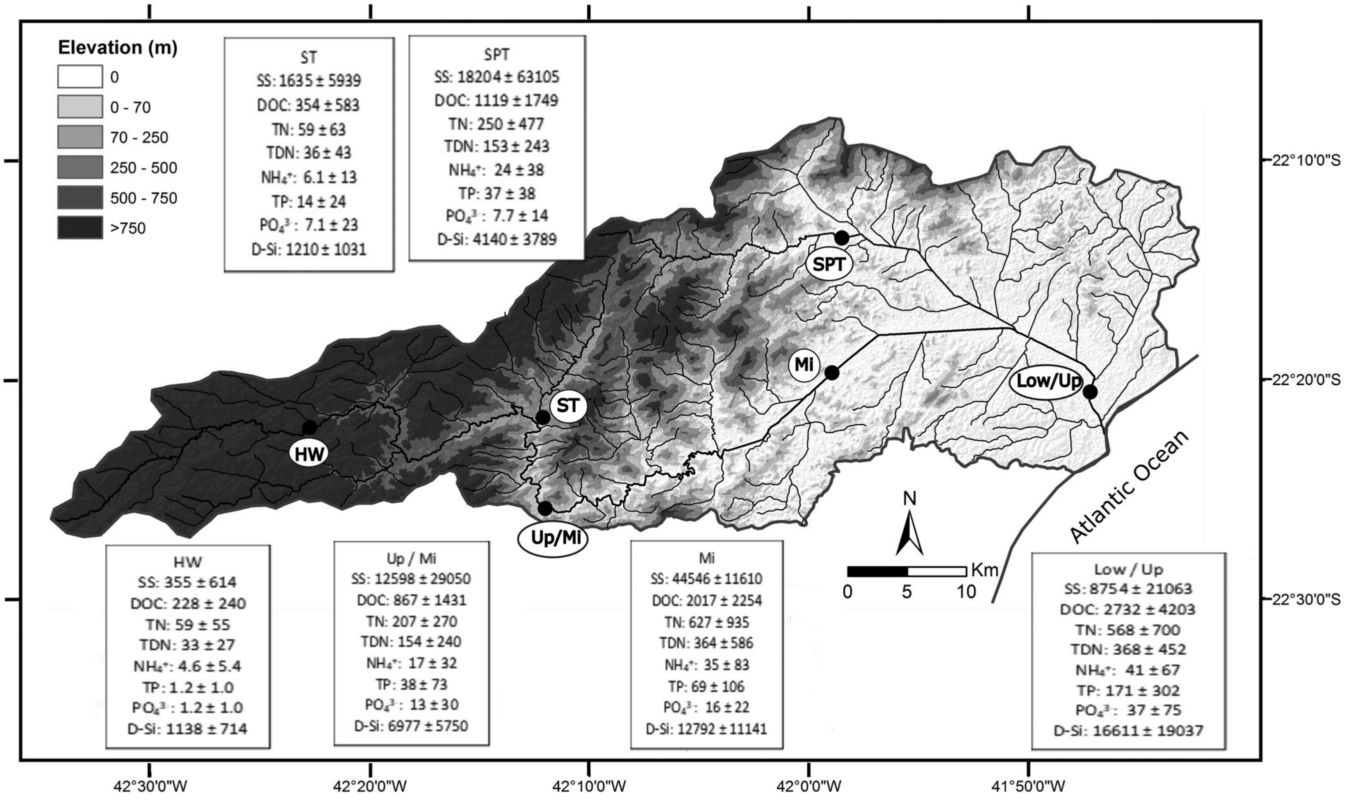

FIGURE 4 Mean biannual fluxes ± *SD* (t y^{-1}) of suspended sediment and nutrients transported along the main channel (HW, Up/Mi, Mi, Low/Up) and Sana (ST) and São Pedro (SPT) tributaries of the Macaé River basin

statistically different between TN and TDN ($p < .05$), representing a twofold to threefold higher flux compared to 2013–2014 (Table 3).

Although river discharge, sediment and nutrient fluxes indicated greater (SS and TN), less (D-Si, DOC, TDN, NH_4^+) or no retention (TP and PO_4^{3-}) influence by the coastal plain, the coastal plain and lower river and upper estuary experienced the highest river discharge, DOC, TN, TDN, NH_4^+, TP, PO_3^- and D-Si yields. Only the suspended sediment had lower yields in the coastal plain, primarily within the lower river/upper estuary.

4 | DISCUSSION

The sediment load (0.04×10^6 t year^{-1}) and yield (85 t km^2 year^{-1}) from the small Macaé River were in the same range (load: 0.01–10 × 10^6 t year^{-1}; yield: 10–1,000 t km^2 year^{-1}) reported for other small coastal basins (0.001×10^6 km^2 area) around the world with low or no human impact (Milliman & Syvitski, 1992; Vanmaercke, Poesen, Broeckx, & Nyssen, 2014; Warrick, Madej, Goñi, & Wheatcroft, 2013). The annual nutrient concentrations and fluxes of the Macaé River were of the same order of magnitude as those reported from other South-east Atlantic basins, including forested and well-preserved watersheds with low human occupation (Andrade et al., 2011). Considering that our results are in the same range of the material fluxes and yields from other small coastal basins, and given that we present results about the influence of coastal plain on material fluxes, we thought that for a small mountainous coastal watersheds there would be an influence of the coastal plain on seaward material fluxes, including retention of sediments and nutrient export caused by anthropogenic inputs. However, few studies have quantified material retention capacity across the entire coastal plain of such small watersheds (Goldsmith et al., 2015; Lyons et al., 2002; Moyer et al., 2015).

When comparing the N, P and Si fluxes of the Macaé River and other coastal watersheds to global comparisons, such fluxes were 4–5 orders of magnitude lower than that observed in larger rivers (Turner, Rabalais, Justic, & Dortch, 2003). Although small basins export at least four orders of magnitude less nutrients and suspended sediment fluxes than large rivers, such small watersheds can locally affect coastal environments. Even the sediment retention within the river's coastal plain is limited given that, suspended sediment loads from the Macaé River have been recognized to contribute to siltation of coral reefs, located 44 km away from the basin mouth (Godiva, Evangelista, Kampel, Licinio, & Munita, 2010). This clearly highlights the importance of peak discharge, which influences the retention capacity across the coastal plain.

The resulting river–ocean fluxes and effects of such small river basins reflect the downstream changes along the basin and the influence of the coastal plain and upper estuary on river fluxes. From upstream to the middle river, relief ranges from 1,570 to 100 m, and the slope from 288 to 1.0 m km^{-1} along a channel 74 km in length. In the last 62 km across the coastal plain, the slope ranges from 0.38 to 0.04 m km^{-1} (Marçal et al., 2017). As slope attenuates in downstream direction, mean discharge velocity is also reduced, but did not affect DOC, nitrogen and TP concentrations observed along the 136-km river channel. Thus, the different morphology from upstream to the coastal plain and upper estuary did not influence patterns of nutrient concentrations of a small mountainous coastal basin. The geomorphology and short water residence times of small basins have also been used to explain homogenous nutrient concentrations in river channels (Jennerjahn et al., 2008; Moyer et al., 2015). However, when the river flows across the coastal plain and reaches the upper estuary, the water velocity is reduced and suspended sediment concentrations decreased (inducing particle deposition and increasing chlorophyll *a* and phytoplankton biomass). Thus, the influence of tides (upper estuary) on the lower river basin appears to be important for primary production, as described for other small basins (Roegner, Seaton, & Baptista, 2011), although in the Macaé River this only occurred during the dry season.

For small mountainous coastal watersheds, basin area and maximum elevation explain most of the land–sea transport, which may also explain a secondary relationship with land-use change, climate and geology (Milliman & Syvitski, 1992; Overeem, Kettner, & Syvitski, 2013; Warrick et al., 2013). In the study basin, higher fluxes were observed across the steeper slope gradient from upstream areas to the upper/middle river, with suspended sediment more efficiently transported. From the middle basin to the lower river/upper estuary, transport efficiency was lower, demonstrating the influence of the coastal plain and tides on reducing material fluxes prior to coastal export. This reflects the patters of DOC reported from other subtropical small basins (Moyer et al., 2015). Suspended sediment flux reduction across the coastal plain may be interpreted as reduced erosion, as confirmed by the lower sediment yields in the Macaé River reach, and as shown in a study that described sediment trapping and storage in alluvial sites upstream of estuaries (Slaterry & Phillips, Slattery & Phillips, 2011). In addition, the lowest water velocities measured in the upper estuary also contributed to the suspended sediment deposition and flux reduction in the lower river and upper estuary. The fluvial material retention across the coastal plain occurs in the last 26 km of the river, even though the section has been artificially straightened, reducing the sinuosity index, from 1.58 (sinuous channel) to 1.01 (straight channel) (Marçal et al., 2017). However, river straightening may favour episodic high discharge that collapse the estuarine barrier and transfer material directly into the sea, (e.g., March 2013), although coastal plain area also acts to reduce material fluxes.

Higher seaward transfer of TP and PO_4^{3-} fluxes may be associated to the influence of anthropogenic sources, probably cattle and domestic sewage, as main nutrient sources located across the coastal plain (Molisani, Esteves, Rezende, & Lacerda, 2013). Total P in domestic sewage is present in the form of inorganic orthophosphates, with the main source being detergents and other household chemical products, as well as in human faeces, urine and food remains (IAWQ, 1995). For cattle, typically 45–90% of manure P is inorganic, which is usually water soluble, and makes it very mobile and susceptible to runoff, increasing total P inputs into aquatic ecosystems (Sharpley & Moyer, 2000). As proposed by Tysmans et al. (2013), nutrient retention within a drainage basin or export to the ocean is largely a function of loads emitted from both natural processes and anthropogenic sources. As river basins provide elevated nutrient inputs, mainly due to human sources, efficient seaward transport is usually expected. In this context, Molisani et al. (2013) calculated nitrogen and phosphorus emissions from natural processes (soil erosion and atmospheric deposition) and anthropogenic sources (urbanization, agriculture, animal husbandry) across the Macaé River basin. The estimated N and P emissions, of 1,599 and 787 t y^{-1}, respectively, predominately originated from anthropogenic emissions (90 and 99% of total, respectively), mainly from untreated domestic waste and animal husbandry. Land use, as well as land cover, is comprised, predominantly, of Atlantic Forest in upstream reaches, while in downstream areas, pasture, urbanization and arable agriculture take place across the middle basin and lower river/upper estuary (Molisani et al., 2019). The estimated TN and TP emissions and measured fluxes of 735 and 146 t y^{-1}, respectively, at the basin outlet, indicate that about 54% of N and 81% of P are largely retained within the basin. Retention occurs in soils where animal husbandry and waste waters release into septic tanks are disposed of, and P storage in soils may be an important source and pathway for transferring particulate (and also soluble) phosphorous to the river channel and increasing P concentrations and fluxes across the coastal plain and upper estuary. The statistically positive correlation between PO_4^{3-} and suspended sediment and DOC in the lower river/upper estuary supports the influence of coastal plain soils and both anthropogenic and natural sources on increased P fluxes.

The findings presented herein indicate that the coastal plain of a small mountainous coastal basin both reduced the downstream increases of DOC, TDN, NH_4^+, D-Si fluxes, and curbed suspended sediment and TN fluxes, mainly in the lower river/upper estuary. In contrast, TP and PO_4^{3-} fluxes sharply increased across the coastal plain, suggesting that river processes, involving suspended sediment and DOC, as well as, anthropogenic and natural inputs, may be more important than the geomorphological controls for material fluxes. Tributaries contribute significantly to the material fluxes both in the mountainous and coastal plain reaches of this small coastal catchment. However, the coastal plain did not affect nutrient concentrations, but did reduce turbidity, and increased chlorophyll *a* and primary productivity in the lower river and upper estuary during the dry season. Even with narrow coastal plain areas, small catchments retain sediment and nutrients within the lower river basin and estuary, including during periods of high discharges, controlling the material export to the sea. In addition, the coastal plain area and adjacent coastal zone may be susceptible to eutrophication and siltation due to nutrient and particle accumulation.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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