http://dx.doi.org/10.21577/0100-4042.20230058 *Quim. Nova,* Vol. 46, No. 6, 616-626, 2023

LONG-TERM TREND OF NITROGEN AND PHOSPHORUS TRANSPORT IN 12 TROPICAL COASTAL WATERSHEDS IN NORTHEAST BRAZIL

Carlos Noriega[a,b,c,*], **Moacyr Araujo**[a,b,c], **Humberto L. Varona**[a,b], **Mauricio Costa**[c], **Amilcar E. Calzada**[a], **Carmen Medeiros**[a], **Andrea Xavier Silva**[d], **Livia P. Portela**[d], **Daniella S. Bezerra**[d], **Rivaldo Jeronimo**[d], **Paulo P. Barros**[d], **Julia Araujo**[e] **and Marcelo Rollnic**[f]
[a]Departamento de Oceanografia, Universidade Federal de Pernambuco, 50740-550 Recife – PE, Brasil
[b]Centro de Estudos e Ensaios em Risco e Modelagem Ambiental (CEERMA), Universidade Federal de Pernambuco, 50740-550 Recife – PE, Brasil
[c]Rede Brasileira de Pesquisas sobre Mudanças Climáticas Globais (Rede CLIMA), 12227-010 São José dos Campos – SP, Brasil
[d]Agência Estadual de Meio Ambiente - CPRH, 52061-340 Recife – PE, Brasil
[e]Instituto Oceanográfico da Universidade de São Paulo, 05508-120 São Paulo – SP, Brasil
[f]Departamento de Oceanografia, Universidade Federal do Pará, 66075-110 Belém – PA, Brasil

Recebido em 05/12/2022; aceito em 15/03/2023; publicado na web 24/05/2023

Multiple environmental problems are caused by the accumulation of nitrogen (N) and phosphorus (P) in river water on its way to the ocean. The objective of this work was to determine the N and P loads in 12 hydrographic basins that flow into estuaries along the northeastern coast of Brazil using established methods. Additionally, natural and anthropogenic loads trends in the hydrographic basins of 12 tropical rivers in northeastern Brazil over 27 years (1990-2016) were evaluated. The results indicated an annual average increase of +1.1% in population density, while precipitation showed no significant trend. The anthropogenic loads were 21 and 112 times higher than natural inputs for N and P, respectively. Anthropogenic sources accounted for ~ 96% of all contributions. The positive trends of these loads (mainly wastewater) represented an annual average increase of 1.1% for N and 1.2% for P, for all river basins included in this study. These percentages represent average annual loads of 251 t N yr^{-1} and 54.8 t P yr^{-1}. The time series of N and P in the study region showed trends that point to a constant increase, implying a greater contribution of these loads to the adjacent coastal region year after year.

Keywords: tropical rivers; temporal series; nitrogen; phosphorus; anthropogenic sources.

INTRODUCTION

Rivers and streams are the main pathways by which terrestrial and atmospheric carbon (particulate carbon-PC), nitrogen (N), phosphorus (P), and other elements are delivered to coastal marine areas.[1] The general properties of river systems tend to reflect a combination of geomorphological attributes modified by a wide range of direct and indirect climatic and human influences.

Human activities have greatly changed the flow of substances into coastal marine areas.[2] Multiple problems (including, eutrophication, harmful algal blooms, hypoxia, fish kills) are caused by the accumulation of N, P, and other elements in river water in route to the ocean.[3] Various activities can potentially generate nutrients along the coast: wastewater production, including the release of untreated sewage, agriculture, livestock, soil erosion, and industrial processes. Quantifying nutrient loads provides important information about biogeochemical processes in rivers, estuaries, and the downstream coastal zone.

Tropical rivers and streams are valuable resources, but pollution from urban and agricultural areas poses a threat to their water quality. There has been little quantification of the nutrient loads from coastal drainage basins in northeastern Brazil.

Quantifying nutrient loads provides important information about biogeochemical processes in estuaries and the coastal zone. The objective of this work was to determine the N and P loads from 12 hydrographic basins (24,403 km^2) that flow into the estuaries along the northeastern coast of Brazil, considering both natural and anthropogenic sources from 1990-2016. Additionally, this work's objective was to determine how hydrographic basins have changed with alterations (natural and anthropogenic) over 27 years.

METHODS

Study area

The state of Pernambuco occupies an area of 98,938 km^2, which represents approximately 6% of the area of northeastern Brazil and 1.2% of the total territory of the country. The state has 187 km of coastline and is home to 12 major coastal rivers that flow toward the Atlantic Ocean.[4] These rivers, which were the focus of our study, are Goiana-GO, Botafogo-BF, Igarassu-IG, Timbo-TB, Paratibe-PB, Beberibe-BE, Capibaribe-CB, Jaboatão-JB, Pirapama-PP, Ipojuca-IP, Sirinhaem-SI, and Una-UN (Figure 1).

The 12 systems differ by almost two orders of magnitude in area, from the larger Capibaribe (7,757 km^2) basin to the smaller Beberibe (80 km^2) basin. They are mostly short systems with lower basins located within the "Tabuleiros Costeiros do Nordeste" formation, which is characterized by Tertiary and Quaternary sediments that form coastal plains constituted by sandy soils closer to the coast and yellow-red latosols and podsols inland. Small stretches of alluvial eutrophic soils occur along river valleys.[5] The longer system (Ipojuca River) crosses semi-arid inner areas where it can be intermittent (depending on the amount of rainfall), but it is perennial along its more coastal reach. Rainfall varies from ~ 2,000 mm yr^{-1} on the coast to < 500 mm yr^{-1} in the interior valleys (semi-arid).[6]

The natural vegetation in most of the area has been converted into land for non-mechanized subsistence agriculture and pastureland. The

---

*e-mail: carlos.delnor@gmail.com

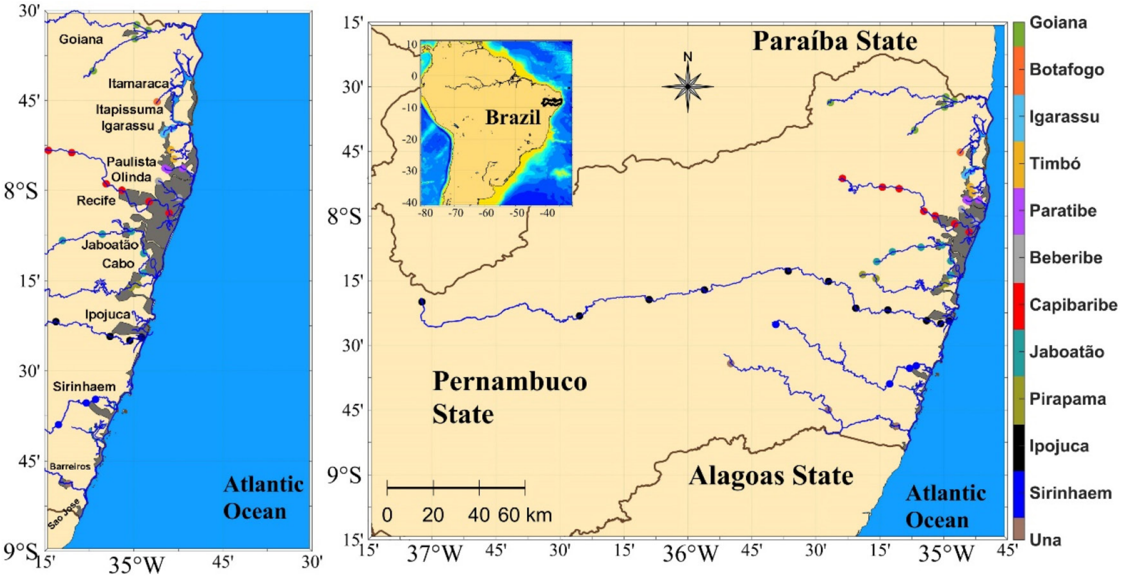

Figure 1. Map showing the locations of the 12 studied river basins in northeastern Brazil. The colored circles indicate monitoring stations in each river. The colors in the sidebar show the geographic location of the sampling stations according to the different rivers. The major cities are highlighted in the left panel

major crops in the sandy soils are coconut and banana, whereas the latosols are used mostly for sugar cane and pasture. Population density is generally high (> 1,000 persons *per* km^2) and is concentrated in cities near the sea (see in the left panel of Figure 1; Paulista, Olinda, Recife, Jaboatão). Industrial activities are located mainly in areas near the shore. Most urban waste is not treated, and agriculture and livestock production have recently intensified along the coastal region. Therefore, prior data already suggest that some of these areas are showing signs of incipient eutrophication.[7] Table 1 shows the environmental characteristics of the 12 rivers studied.

Emission factors methods

The loads associated with the natural edaphic and atmospheric processes were estimated by taking into account the composition and distribution of soils, rates of release and/or retention of the substances of interest in the soil types, and soil loss equations. The main nutrients with high eutrophication potential (N and P) were obtained through coefficients reported in the literature. The contribution of natural N and P emissions through atmospheric deposition was obtained by the average atmospheric deposition,[12-14] weighted by the actual annual rainfall on the river basins (mm) and corrected by factors of retention of each element in the soil (N: 0.37; P: 0.30).[15,16]

$$[N; P]\text{atm.dep}\ (\text{t yr}^{-1}) = E[50; 4.3] \times F[0.37; 0.3] \times R/1000 \times (A) \quad (1)$$

where, [N; P] atm.dep is the total load of N or P via atmospheric deposition in t yr^{-1}; E is the average deposition of [N; P] in mg m^2 yr^{-1}, for rainfall of 1,000 mm; F is the retention factor [0.37; 0.30]; R is the rainfall over the period for the hydrographic basin in mm yr^{-1}, and A is the area of the river basin in km^2. The contribution of natural N and P emissions from physical and chemical denudation of soils was obtained by the factors indicated at for tropical soils.[13,14]

$$[N; P]s.r.(\text{t yr}^{-1}) = A \times M \times E[N; P] / 1 \times 10^9 \quad (2)$$

where, [N; P] s.r. is the total load of N or P via soil runoff in t yr^{-1}; A is the area of the hydrographic basin in km^2; M is the soil loss

Table 1. Environmental parameters that characterize the coastal basins of the state of Pernambuco

River basin	Basin area[a] (km^2)	Annual rainfall[b] (mm)	Basin population[c] (inhabitants)	Density (pop km^{-2})	Fluvial discharge[d] (m^3 s^{-1})	Main type of soil[e] (%)
Goiana - GO	2,878	1,400	567,000	197	20.0	Podsols (66)
Botafogo - BF	280	1,500	178,000	636	6.0	Podsols (42)
Igarassu - IG	143	1,600	114,000	796	3.0	Podsols (41)
Timbo - TB	104	1,600	226,000	3,090	15.0	Podsols (40)
Paratibe - PA	118	1,800	443,000	3,750	3.0	Podsols (42)
Beberibe - BE	80	1,900	675,000	8,338	2.0	Podsols (62)
Capibaribe - CB	7,557	1,400	1,843,000	244	25.0	Planosols (25)
Jaboatao - JB	422	1,500	618,000	1,465	6.0	Latosols (45)
Pirapama - PP	600	1,400	966,000	1,610	7.0	Latosols (46)
Ipojuca - IP	3,514	1,300	615,000	175	12.0	Regosols (35)
Sirinhaem - SI	3,070	1,600	225,000	109	30.0	Latosols (82)
Una - UN	6,293	1,400	679,000	107	35.0	Latosols (32)

[a]Watersheds area.[7] [b]Rainfall series.[8] [c]Density obtained for the basin population/basin area.[9] [d]Fluvial discharge data.[10] [e]Classification of Brazilian soils.[11] The basin codes are also shown.

(12 kg yr^{-1}), and E is the loss factor of the element [N; P] in t yr^{-1} with the loss factors for each type of soil.[13,14]

To estimate loads from anthropogenic sources, the relationships between productive activities and their respective load of elements released into the environment are sought, such relationships are obtained using data on the production and use of agricultural inputs, volumes, and concentrations available for effluents, and retention rates in soils in the basin.[13] Nutrient loads to industrialized coastal watersheds are mostly from diffuse sources and therefore are difficult to directly measure. For this study, we instead used indirect approaches based on emission factors as previously described.[7,14] We used emission factors available in the literature for each separate activity or process. However, all emission factors were adapted to local conditions as needed. For example, correction factors were used to adjust for semi-arid conditions to better estimate actual water consumption rates by the population in each basin.[14]

Emission factors for anthropogenic activities are based on the latest population data available (1990 census; 2016 population estimates) and factors indicated by Bidone and Lacerda, and Bidone.[17,18] Urban runoff depends on the area of impermeable surfaces, the number and size of buildings, annual rainfall and the urban area.[6,19]

Nutrients emitted from livestock are released into soils as animal excrement, and their nutrient contributions depend on the types of animals raised in a region and the concentration of nutrients in their feed. The average values and ranges of excretion for horses, cattle, pigs, poultry, and sheep, as well as the rates of retention of nitrogen and phosphorus in soil and bodies of water were estimated through coefficients.[14]

The industrial loads of N and P were calculated using the Load Organic Remaining method (t BDO d^{-1})[6] and the coefficients were found by SanDiego-McGlone *et al.*[20] N and P contributions from sugarcane cultivation were estimated using the area of cultivation, fertilization practices, and loss of N and P. Data on the area of cultivation,[9] fertilization information,[16] and loss of nutrients[11] were derived from previous studies and coefficients for tropical areas. The potential for environmental degradation-PED is defined as the deterioration in environmental quality from ambient concentrations of pollutants and other activities and processes such as improper land use and natural disasters.[7] The PED in the region was determined by calculating the sum of loads from atmospheric deposition and soil erosion and leaching based on soil physics and chemistry (Level-Based Natural) (NBN). Three levels were proposed: high (> 20 times NBN), medium (2-20 times NBN), and low (< 2 times NBN).[7,14]

Statistical analysis

The statistical analysis used in this work were as follows:

Descriptive statistics: The mean, standard deviation, minimum, maximum, and percentages were calculated. Nonparametric statistics: The Mann-Whitney test was used to verify significant differences between 2 sample sets. The statistics for the time series were calculated using the Mann-Kendall trend test. In the Mann-Kendall test, a trend is considered negative or positive, indicating a decrease or increase in the attributes of the historical series analyzed, if the Mann-Kendall (Kendall's tau) score is negative or positive, respectively. In addition, the trend indicated by this methodology is considered significant when the p-value has a value less than $\alpha = 0.05$. All statistical analysis were performed using mStatGraph v1.0 software.[21]

RESULTS

Rainfall and population density

As indicated above, rainfall varies from ~ 2,000 mm yr^{-1} on the coast to < 500 mm yr^{-1} in the interior valleys (semi-arid),[6] while, the population density in the river basins varies between 100-8000 inhabitants km^{-2} (Table 1). Figure 2 indicates the time series increment rate (1990-2016) for all basins in this study, for rainfall, and population density. The results indicated an annual average increase of +1.1% in population density, while precipitation showed no significant trend (Kendall test; $p > 0.05$). The time series indicated a significant trend for population density (Mann-Kendall test; $p = 0.000006$; $\alpha = 0.05$) and not significant for rainfall (Mann-Kendall test; $p = 0.2$; $\alpha = 0.05$). Differences between historical rainfall (1976-2016) and the study period (1990-2016) were not observed (Mann-Whitney test; $p > 0.05$; α: 0.05).

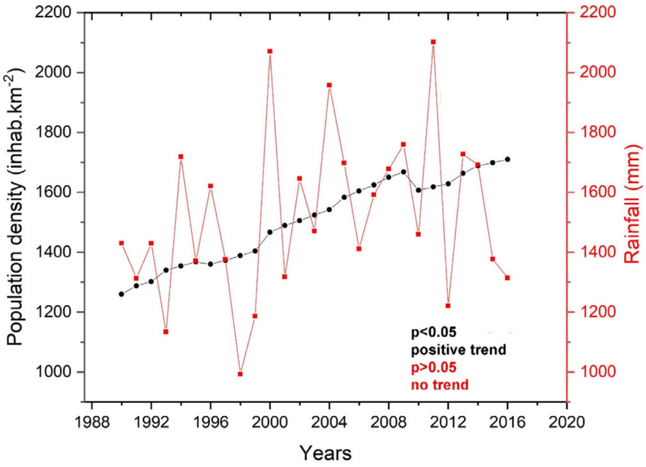

Figure 2. *Time series increment rate (1990-2016) for all basins in this study, for rainfall, and population density. The p symbol indicates the result of the Kendall trend test. The values used correspond to the average annual values of rainfall and population density for all the river basins in this study*

Natural emissions

Soil erosional and leaching loss dramatically increases with agriculture and depends on the soil type and climate, while, atmospheric deposition is a function of the basin area, annual rainfall, and the concentration of N and P in bulk deposition (dry and wet).[7] Losses of N and P (atmospheric deposition + soil runoff) in basins ranged from 8.8 to 726.0 t yr^{-1} and 1.2 to 28.0 t yr^{-1}, respectively (Table 2). Across all basins, 72% of N was due to soil and 28% was due to atmospheric deposition. For P, the distribution was 52% and 48%, respectively. Inputs of N and P were higher in the CB (Capibaribe River) and UN (Una River) basins, which have the largest areas (Tables 1 and 2).

Anthropogenic loads

The total anthropogenic loads of N and P for each basin studied are presented in Table 2. These estimates show N inputs varying from 797 to 43,650 t yr^{-1} and P inputs varying from 215 to 1,685 t yr^{-1}, with maximum values at the CB (Capibaribe) and GO (Goiana) basins. Wastewater was a major source of nutrients to coastal areas, accounting for 50% of N and 44% of P among all natural and anthropogenic sources combined. The second-highest source of contributions was agriculture (sugar cane cultivation; 15,352 and 4,315 t yr^{-1} of N and P, respectively), accounting for ~ 34% and 41% of all natural and anthropogenic contributions in the region, respectively (Table 2).

Total natural loads were 2,069 and 93 t yr^{-1} for N and P respectively, while total anthropogenic contributions were 45,719 and 10,568 t yr^{-1} for N and P, respectively. These values showed that anthropogenic inputs were 21 and 113 times higher than natural inputs for N and P, respectively. Anthropogenic sources accounted for ~ 96% of all loads.

The main anthropogenic nutrient source was urban use (wastewater, urban runoff) with 0.9 and 0.2 t km^{-2} yr^{-1} of N and P, respectively; followed by agriculture (sugar cane) with 0.6 and 0.2 t km^{-2} yr^{-1} of N and P, respectively.

Long-term load trends - N

The time series of natural and anthropogenic N loads are shown in Figures 3 to 5. The results of the time series of atmospheric deposition + soil runoff (Figure 3) did not show a statistically significant trend for the period 1990-2016 in the watersheds of this study (Mann-Kendall test; $p = 0.08$; $\alpha = 0.05$). The anthropogenic N contributions that showed significant positive trends according to the Mann-Kendall test ($p < 0.05$; $\tau = +$ or $-$; $\alpha = 0.05$) were: wastewater ($p = 0.0001$; $\tau = +0.98$), industry ($p = 0.0001$; $\tau = +0.94$) and urban runoff ($p = 0.001$; $\tau = +0.43$); while negative trends were observed in livestock ($p = 0.004$; $\tau = -0.39$) and agriculture ($p = 0.0001$; $\tau = -0.68$).

In Figure 3c and Figure 3l, the largest N contributions by atmospheric deposition and soil runoff were in the Una River (UN) and Capibaribe River (CB) watersheds, while the largest N loads of anthropic origin were: wastewater and agriculture. The high loads via wastewater originated mainly through the Capibaribe River (CB), Pirapama River (PP) and Beberibe River (BE) basins. The N load through wastewater in the Beberibe River basin (BE) reached 92% of the total loads of natural and anthropic origin (Figure 4 and Table 2).

N contributions from agricultural sources (Figure 5) showed high loads in the watersheds of the Goiana River (GO) and Sirinhaem River (SI), while the smallest contribution was from the Paratibe River (PA), as indicated in Figure 5d, Figure 5j, and Figure 5h, respectively. N emissions through livestock showed higher inputs in the Jaboatão (Figure 5g) and Pirapama (Figure 5i) rivers. According to the statistical analysis (indicated above), agriculture and livestock showed negative trends in the N time series (Figure 5).

Long-term emissions trends - P

The time series of natural and anthropogenic P loads are shown in Figures 6 to 8.

The results of the time series of atmospheric deposition + soil runoff (Figure 6) did not show a statistically significant trend for the period 1990-2016 in the watersheds of this study (Mann-Kendall test; $p = 0.07$; $\alpha = 0.05$). The anthropogenic P contributions that showed significant positive trends according to the Mann-Kendall test ($p < 0.05$; $\tau = +$ or $-$; $\alpha = 0.05$) were: wastewater ($p = 0.0001$; $\tau = +0.99$), industry ($p = 0.0001$; $\tau = +0.95$) and urban runoff ($p = 0.0001$; $\tau = +0.42$); while negative trends were observed in livestock ($p = 0.002$; $\tau = -0.42$) and agriculture ($p = 0.0001$; $\tau = -0.70$).

Table 2. Estimates of N and P loads (t yr^{-1}) from natural and anthropogenic sources in basins in northeastern Brazil. The relative contribution (%) of each individual source is in parenthesis

Basin	Natural sources		Anthropogenic sources					Total
	Soil runoff	Atmospheric deposition	Wastewater	Urban runoff	Industrial	Livestock	Agriculture (sugar cane)	
GO N	176 (2)	73 (1)	1,907 (28)	4 (< 1)	978 (14)	133 (2)	3,784 (56)	7,054
GO P	9.8 (< 1)	5 (< 1)	381 (23)	0.8 (< 1)	216 (13)	62 (3.7)	1,025 (61)	1,700
BF N	21 (1)	8 (< 1)	528 (33)	0.6 (< 1)	21 (1.3)	80 (5)	951 (60)	1,610
BF P	3 (< 1)	0.5 (< 1)	106 (26)	0.1 (< 1)	4.6 (1.1)	45 (11)	251 (62)	410
IG N	11 (1)	4 (< 1)	333 (42)	1.5 (< 1)	13 (1.6)	115 (14)	334 (42)	812
IG P	2 (< 1)	0.3 (< 1)	67 (31)	0.3 (< 1)	2.9 (1.3)	76 (35)	69 (32)	217
TB N	8 (1)	3 (< 1)	995 (65)	1.8 (< 1)	27 (1.8)	132 (9)	370 (24.2)	1,537
TB P	1.1 (< 1)	0.2 (< 1)	199 (54)	0.4 (< 1)	6.1 (1.6)	68 (18)	98 (26.3)	373
PA N	9 (1)	4 (< 1)	1,403 (94)	3.4 (< 1)	55 (3.7)	29 (2)	0 (0)	1,503
PA P	1 (< 1)	0.3 (< 1)	281 (91)	0.7 (< 1)	12.1 (4)	16 (5.2)	0 (0)	311
BE N	6.8 (< 1)	2.7 (< 1)	2276 (92)	4.3 (< 1)	89 (4)	78 (3)	31 (1.3)	2,489
BE P	2 (< 1)	0.2 (< 1)	455 (86)	0.9 (< 1)	20 (3.8)	46 (9)	8 (1.5)	532
CB N	397 (5)	196 (2.5)	5,476 (79)	19 (< 1)	133 (2)	136 (2)	1,241 (17)	7,868
CB P	9 (1)	13.6 (< 1)	1,149 (69)	4 (< 1)	29.3 (1.8)	63 (3.8)	420 (25.2)	1,687
JB N	30 (1)	11.4 (< 1)	1,973 (49)	2.5 (< 1)	271 (7)	196 (4.9)	1,595 (40)	4,079
JB P	3 (< 1)	0.8 (> 1)	395 (40)	0.5 (< 1)	60 (6.1)	105 (11)	422 (43)	986
PP N	44 (1)	16 (< 1)	2,982 (61)	1.9 (< 1)	46 (1)	137 (2.8)	1,721 (35.2)	4,948
PP P	4 (< 1)	1.1 (< 1)	596 (53)	0.4 (< 1)	10.1 (< 1)	70 (6.2)	458 (40.3)	1,139
IP N	219 (8)	8 (< 1)	1,874 (70)	3.7 (< 1)	115 (4.3)	111 (4)	562 (21)	2,893
IP P	4 (1)	5.7 (< 1)	375 (58)	0.8 (< 1)	25.5 (4)	48 (7.4)	200 (31)	659
SI N	155 (3)	59 (1.1)	719 (14)	0.7 (< 1)	1,402 (28)	79 (1.6)	2,798 (56)	5,213
SI P	4 (< 1)	4.6 (< 1)	144 (33)	0.1 (< 1)	310 (25)	31 (2.5)	768 (61.2)	1,262
UN N	440 (8)	167 (3)	2,102 (41)	2.1 (< 1)	906 (18)	133 (2.6)	1,965 (38)	5,715
UN P	7 (1)	11.6 (1)	420 (44)	0.4 (< 1)	200 (16)	56 (4.4)	596 (47)	1,291
Total N	1,517 (3)	552 (< 1)	22,838 (50)	45.1 (< 1)	4,056 (8.8)	1,359 (3)	15,352 (34)	45,719
Total P	49 (< 1)	44 (< 1)	4,568 (44)	9.4 (< 1)	897 (8.5)	686 (6.5)	4,315 (41)	10,568

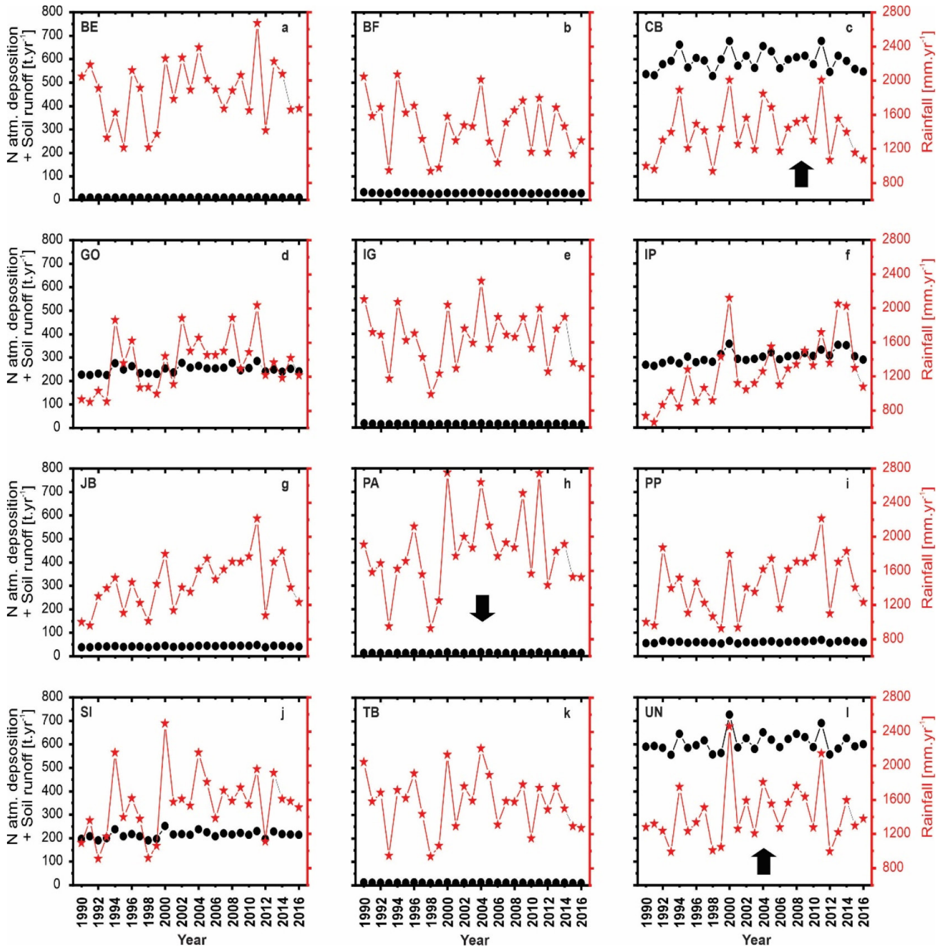

Figure 3. Temporal series (1990-2016) of atmospheric N deposition + soil runoff (black line) and rainfall (red line) in the hydrographic basins (a)-(l). Arrows indicate the watersheds with the highest and lowest contributions

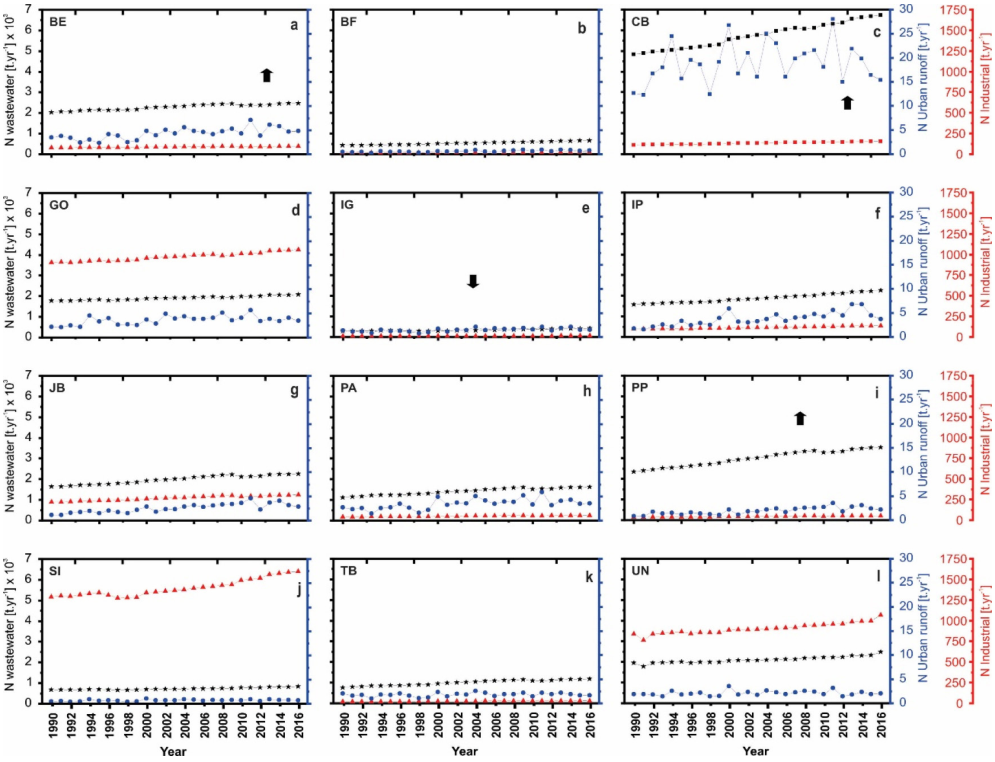

Figure 4. Temporal series (1990-2016) of N wastewater (black line), industry (red line) and urban runoff (blue line) in the hydrographic basins (a)-(l). Arrows indicate the watersheds with the highest and lowest contributions

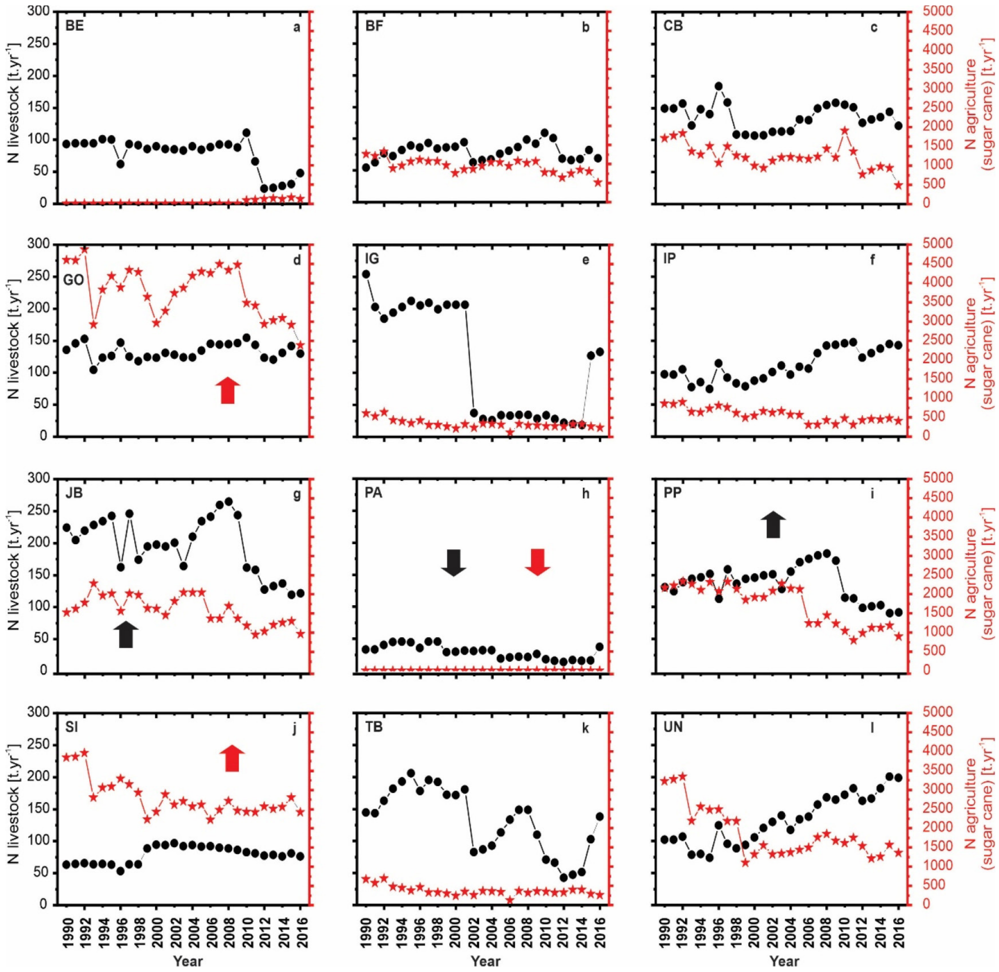

Figure 5. *Temporal series (1990-2016) of N livestock (black line) and agriculture (red line) in the hydrographic basins (a)-(l). Arrows indicate the watersheds with the highest and lowest contributions*

Wastewater had the highest P input (44%), where the Capibaribe and Pirapama river basins (Figure 7c and Figure 7i) showed the highest inputs, while the lowest input was observed in the Igarassu River (Figure 7e). P input via urban runoff, in a smaller proportion than wastewater, showed higher contributions from the Capibaribe and Beberibe river basins (Figure 7c and Figure 7a), while P input from industries also represented a low percentage of the total (8.5%; Table 2), concentrating important contributions in the basins of the Sirinhaem and Goiana rivers (Figure 7j and Figure 7d).

Similar to P inputs via industries, livestock loads represented < 10% of the total (Table 2). The watersheds of the Jaboatão and Igarassu rivers showed the highest P inputs to the adjacent estuarine systems (Figure 8g and Figure 8e). P inputs via agriculture represented the second-largest input of anthropogenic contributions (41%; Table 2). The watersheds of the Goiana and Sirinhaem rivers recorded the largest contributions (Figure 8d and Figure 8j). The smallest contributions corresponded to the Paratibe River (Figure 8h) which has a lower ground cover for agricultural activity.

DISCUSSION

Natural emissions

Soil loss and atmospheric deposition are the two major natural processes contributing to N and P loads in the studied basins. Losses from agricultural land in tropical regions average 130 t km^{-2} yr^{-1} for flat land without mechanized agriculture,[22] which characterizes the coastal plains in northeastern Brazil.[7,14] N contributions due to soil loss in temperate climates without mechanized agriculture range from 75 to 230 kg km^{-2} yr^{-1}, with an average of 133 kg km^{-2} yr^{-1}, whereas P loads range from 5 to 50 kg km^{-2} yr^{-1}.[3]

However, recent experiments carried out in southern Bahia-Brazil measured annual rates ranging from 48 to 123 t km^{-2}. The soils in this region (latosols, podzsols) are similar to those observed in our study region (Table 1).

Losses of N and P in the studied basins were within the lower ranges reported for areas with mechanized agriculture (average of 95 and 9 kg km^{-2} yr^{-1} for N and P, respectively). These values are similar to those reported for the Contas and Gongogi river basins in the state of Bahia, Brazil.[13] The loads vary depending on basin size, as was reported for northeastern Brazil by Lacerda.[14] Capibaribe and Una basins had the greatest losses of N and P, respectively. These two basins are the largest in Pernambuco state and together represent 58% of the total area studied.

Along the Brazilian coast, total N and P atmospheric deposition ranges from 80 to 300 mg N m^{-2} yr^{-1} and 4 to 10 mg P m^{-2} yr^{-1} in pristine *vs*. heavy industrial areas, respectively, with an annual rainfall of about 1,000 mm.[22] Deposition also depends on the degree of coastal urbanization and industrialization. Inputs to estuaries from the atmosphere estimated using these parameters were low (average of 30 and 2 mg m^{-2} yr^{-1} for N and P, respectively), and similar values were obtained in the basins of northeastern Brazil (35 and 5.6 mg m^{-2} yr^{-1} for N and P, respectively).[14] Natural source loads studied here are small compared to other urban areas but are similar to values reported in

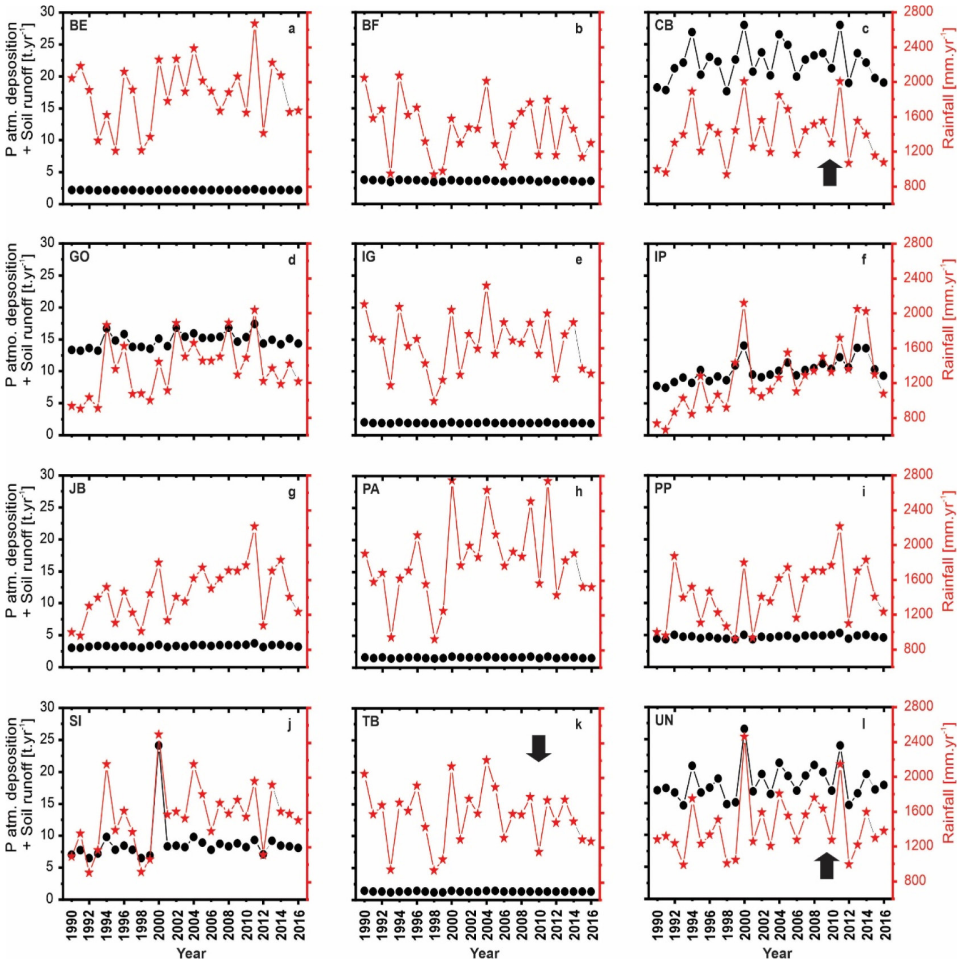

***Figure 6.** Temporal series (1990-2016) of atmospheric P deposition + soil runoff (black line) and rainfall (red line) in the hydrographic basins (a)-(l). Arrows indicate the watersheds with the highest and lowest contributions*

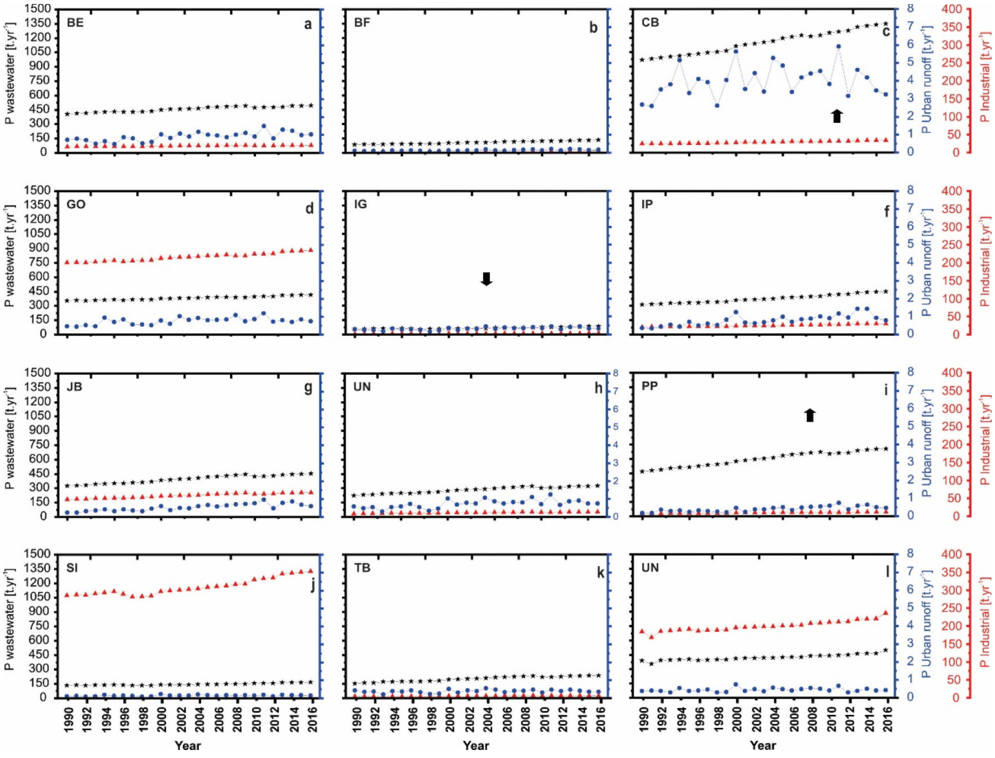

***Figure 7.** Temporal series (1990-2016) of P wastewater (black line), industry (red line) and urban runoff (blue line) in the hydrographic basins (a)-(l). Arrows indicate the watersheds with the highest and lowest contributions*

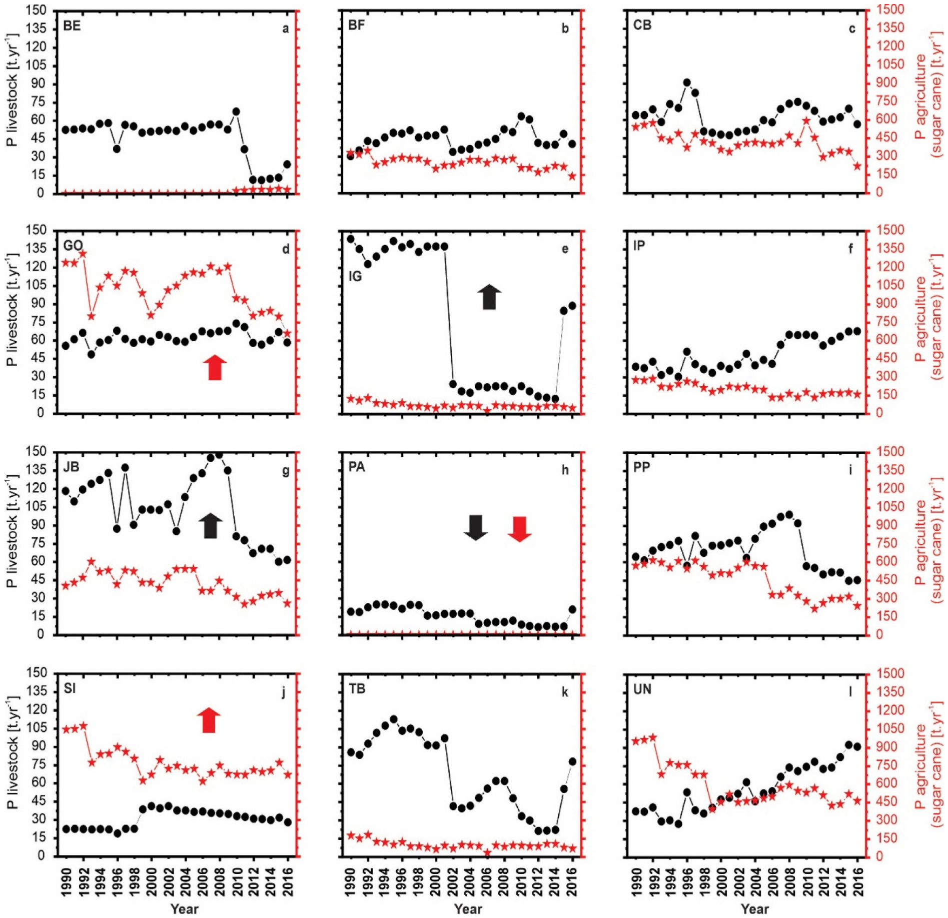

***Figure 8.** Temporal series (1990-2016) of P livestock (black line) and agriculture (red line) in the hydrographic basins (a)-(l). Arrows indicate the watersheds with the highest and lowest contributions*

other areas of northeast Brazil. Estimated loads from natural sources represented ~ 4% of total emissions. Additionally, statistical analysis of the time series of N and P did not show significant trends for the watersheds of this included in this study.

Anthropogenic emissions

The most important anthropogenic sources of N and P were studied here, and their relative contributions varied depending on the degree of urbanization, population, and extent of agricultural lands.

Anthropogenic sources showed similar temporal trends for N and P in the 1990-2016 series. Within the anthropic sources; wastewater and industries recorded the highest contributions of N and P to estuaries in the adjacent coastal region. Accordingly, we can stipulate that the main factor responsible for these positive trends is population growth. The increase in N and P loads were a direct consequence of the population annual growth rate in the study region (1.1%). Additionally, N and P loads via natural sources accounted for < 4% of total contributions. Thus, the anthropogenic loads were 21 and 112 times higher than natural inputs for N and P, respectively. Anthropogenic sources accounted for ~ 96% of all contributions.

The intense population growth, mainly in hydrographic basins with high urban coverage and a low rate of sewage treatment, has increased loads of N and P in the region. The positive trends of these loads (mainly wastewater) represented an annual average increase of 1.1% for N and 1.2% for P, for all river basins included in this study. These percentages represent average annual loads of 251 t N yr^{-1} and 54.8 t P yr^{-1}, respectively. Agriculture is a major source of excess N and P for the coastal region in non-urbanized areas. Generally, clay soils lose 10 to 40% of nutrients applied as fertilizers, while in sandy soils the loss may reach up to 25 to 80%.[23]

The need for N fertilization is particularly high for sugar cane (90 to 275 kg ha^{-1}).[14] Nutrient losses from this crop are 26-32% for N and 6-20% for P.[16] Small basins may receive more N from agriculture. For example, the relatively small basins (Botafogo, Igarassu, Paratibe, Beberibe and Timbo) with 751 km^2, receive more N from agriculture (1,686 t yr^{-1}) than the larger Capibaribe basin (7,557 km^2), which received only 1,241 t yr^{-1} of N, due to the dominance of sugar cane.

The estimated loads, normalized by the total area of the hydrographic basins, showed that N loads reached 1,600 kg N km^{-2} yr^{-1} and 417 kg P km^{-2} yr^{-1}, respectively. These values represent almost double the N reported at the Rio Grande do Norte basins for emissions from agricultural activity;[14] and 7 times that registered in the Ceará region (Figure 9).[24] Additionally, P loads via agriculture also showed high rates when compared to other hydrographic basins in the tropical region. According to our estimates, P loads represented 2.4 times (172 kg P km^{-2} yr^{-1}) the estimates in the Contas River (Brazil),[13] and 1.5 times (266 kg P km^{-2} yr^{-1}) in the Rio Grande do Norte basins.[14] Thus, the contributions of N and P normalized by the area of agricultural activity were higher than other basins in northeastern Brazil. On the other hand, livestock showed similar values when compared to other estimates from tropical regions. The values estimated in this study (368 kg N km^{-2} yr^{-1} and 207 kg P km^{-2} yr^{-1}) are similar to those reported by other authors.[14,24,25]

Nutrients loaded from livestock activity are released to the soil as animal excrement, and their concentration depends on nutrient concentrations in animal feed and on the types of animals raised in a region.[7] Contributions of N and P due to livestock were independent of the basin area. Jaboatão and Igarassu basins are 17 and 52 times smaller than the Capibaribe basin respectively but received more N and P from livestock due to the predominance of poultry.

Inputs due to industrial activity represent 10% of total contributions, and basins with higher industrialization had the highest inputs of N and P, independent of the size of the basin. Significant positive trends of N and P were observed in the study region, including the 12 hydrographic basins. These basins will show increases of ~ 1% (at t yr^{-1}) for N and P, respectively.

Major parameters determining nutrient loss by runoff from urban areas are the area of impermeable surfaces, the number and size of buildings, and annual rainfall.

The results show a direct relationship between N and P loads and the extent of the urban area. The highest estimated N and P loads corresponded to basins with a high urbanization rate (Capibaribe, Beberibe, Paratibe rivers). Rainfall did not contribute much to variation between basins due to the little difference in rainfall totals.

The total urban runoff contribution corresponded to < 1%, similar to the values estimated in Contas River.[13]

Wastewater is one of the major sources of nutrients to coastal areas, particularly in urbanized estuaries.[7,14,24] When no treatment plants exist, nutrient loads from this source are directly proportional to the human population and the amount of water used per inhabitant.[7,25]

The estimates show that N and P inputs due to wastewater are independent of basin size and proportional to the population. The inputs of N and P from wastewater in basins in the state of Pernambuco were higher than other basins in northeastern Brazil (Figure 9).

Basins with a high population, such as Capibaribe, Beberibe and Pirapama, had more emissions than basins with smaller populations. The population density was also highly correlated with N and P loads due to wastewater (r = 0.5; r = 0.7 and r = 0.4, respectively).

The estimated trends showed a positive annual increment of 1.2% for N and P, respectively.

There is a ~ 1% annual population growth rate for this region, which results in an increase in the volume of wastewater every year and an increased nutrient input.

The potential for environmental degradation-PED

The PED (estimated through the levels of natural base and the anthropogenic loads of wastewater and urban runoff) showed high values for N and P in the basins of the study region. Estimated PED levels for N showed 50% of catchments with high PED (n = 6) and 50% of catchments with a medium PED level (n = 6). Low levels of PED (< 2 NBN) were not recorded. Additionally, the P showed 92% of basins (n = 11) with a high level of PED and 8% (n = 1) with medium levels.

The results showed that in basins with high population density, PED levels were higher (Paratibe, Jaboatão, Pirapama, Beberibe) for N and P, respectively. When compared to other regions of northeastern Brazil, the watersheds in this study showed higher levels of PED.

Watersheds in the state of Ceará showed low levels of PED for N and P, respectively (N_{PED} = 1; P_{PED} = 0.5), while in basins of Rio Grande do Norte high and medium PED levels were estimated (N_{PED} = 2.2; P_{PED} = 2). In the Contas River basin, PED levels were low and high for N and P, respectively (N_{PED} = 0.3; P_{PED} = 10).

As indicated above, the estimated PED levels in Pernambuco were high (N_{PED} = 20; P_{PED} = 77), indicating a strong anthropogenic pressure in this region, mainly in river basins with high population density and low levels of sewage treatment.

The timeline of N and P loads showed that loads have steadily increased since 1990, mainly wastewater, as seen in Figure 10. N and P contributions through wastewater have increased by 37% in 27 years; while natural loads increased by 4% and 6%, respectively (Figure 10a and Figure 10b).

The reduction of N and P loads from agricultural activity (~ 50%) is indicative of changes in new agricultural technologies that reduce N and P contributions; but also, in the reduction of the land occupation area for this activity. However, N and P loads via agricultural activities still represent high values when compared to other river basins in the northeast region of Brazil. Additionally, population growth has generated greater urban runoff due to the growth of cities inserted in the watersheds of this study.

CONCLUSION

These results demonstrate that anthropogenic sources (wastewater, industry, livestock, urban runoff, and agriculture) produce sufficient nutrient levels to cause eutrophication and environmental degradation. The results indicated an average annual increase of +1.1% in population density, while precipitation showed no significant trend.

Anthropogenic sources accounted for ~ 96% of all contributions. The time series of N and P in the study region showed trends that point to a constant increment, implying a greater contribution of these

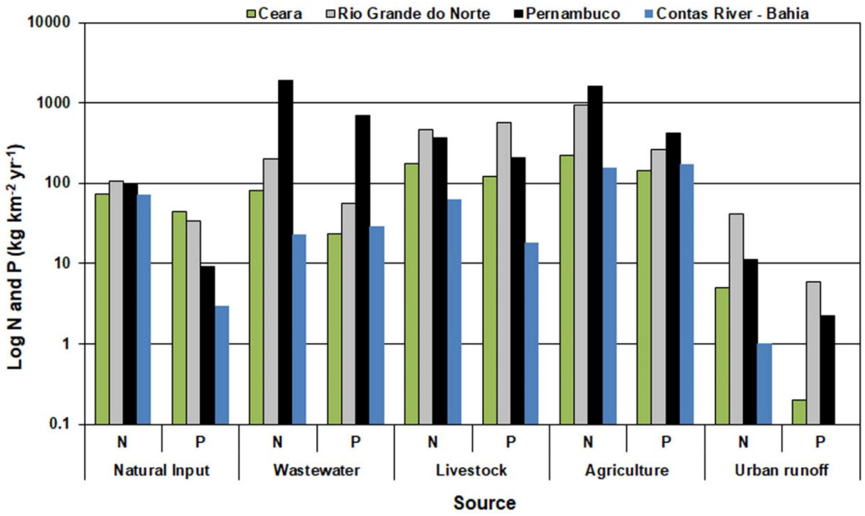

Figure 9. Comparison of N and P loads (kg km^{-2} yr^{-1}) (logarithmic scale) from basins in 4 sites in northeastern Brazil; Ceará State,[14] Rio Grande do Norte State,[25] Contas River,[13] and Pernambuco State

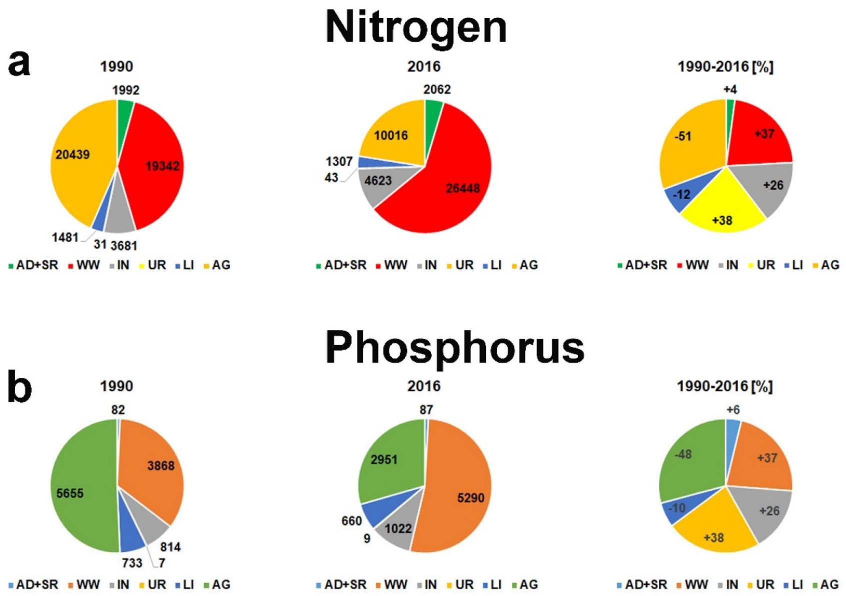

Figure 10. *Sectoral comparison of N(a) and P(b) loads in the study region. (AD + SR): atmospheric deposition + soil runoff; (WW): wastewater; (IN): industry; (UR): urban runoff; (LI): livestock; (AG): agriculture. Values in t yr^{-1} (1990 and 2016) and % (1990-2016)*

loads to the adjacent coastal region year after year. N and P emissions from wastewater have increased by 37% in 27 years, while natural loads increased by 4% and 6%, respectively. High population density basins such as Beberibe, Jaboatão, Paratibe, for example, have 2 and 10 times the upper acceptable limit for urban N and P emissions, respectively. Estimated PED levels showed high levels of N in 50% of the basins studied, while P showed high levels of PED in 92% of the basins in this study. The comparative analysis of the study region with other coastal regions of northeastern Brazil showed higher loads of N and P from wastewater to the Atlantic Ocean in the period 1990-2016. Nutrient levels in these basins are sufficient to generate serious environmental problems in the rivers and adjacent estuarine region.

ACKNOWLEDGMENTS

INCT AmbTropic, Brazilian National Institute of Science and Technology for Tropical Marine Environments, and CNPq/FAPESB provided financial support (Grants 565054/2010-4 and 8936/2011). M. A. and C. N. received support from the Brazilian Research Network on Global Climate Change (Rede CLIMA) (FINEP Grant 01.13.0353-00). C. N. was supported by the National Oil Agency-ANP and the PRH-ANP 38.1 program with grant (process: 044819). H. L. V. acknowledges the TRIATLAS project, which has received funding from the European Union's Horizon 2020 Research and Innovation Program under grant agreement nº 817578 and the International Joint Laboratory TAPIOCA (IRD-UFPE-UFRPE).

REFERENCES

1. Huang, T. H.; Chen, C. T. A.; Tseng, H. C.; Lou, J. Y.; Wang, S. L.; Yang, L.; *Biogeosciences* **2017**, *122*, 1239. [Crossref]
2. da Cunha, L. C.; Buitenhuis, E. T.; Le Quéré, C.; Giraud, X.; Ludwig, W.; *Global Biogeochem. Cycles* **2007**, *21*, 1. [Crossref]
3. Howarth, R.; Anderson, D.; Cloern, J.; Elfring, C.; Hopkinson, C.; Lapointe, B.; *Issues in Ecology* **2000**, *7*, 1. [Link] accessed in April 2023
4. Agência Estadual de Meio Ambiente - CPRH; *Monitoramento das Bacias Hidrográficas de Pernambuco 2001-2005*. [Link] accessed in May 2023
5. Silva, L. F.; *Solos Tropicais: Aspectos Pedológicos, Ecológicos e de Manejo*, 1ª ed.; Terra brasilis: São Paulo, 1996.
6. Agência Estadual de Meio Ambiente - CPRH; *Report on the Monitoring of Water Quality in the Watersheds of the State of Pernambuco in 2016*. [Link] accessed in April 2023
7. Noriega, C.; Araujo, M.; *J. Coastal Res.* **2009**, *56*, 871. [Link] accessed in April 2023
8. National Meteorological Institute (INMET); *Meteorological Database for Teaching and Research – BDMEP*. [Link] accessed in April 2023
9. Brazilian Institute of Geography and Statistics (IBGE), available at www.ibge.gov.br/cidades, accessed in April 2023.
10. Noriega, C.; Araujo, M.; *Sci. Rep.* **2014**, *4*, 1. [Crossref]
11. Santos, H. G.; Jacomine, P. K.; Anjos, L. H.; Oliveira, V. A.; Lumbreras, J. F.; Coelho, M. R.; *Sistema Brasileiro de Classificação de Solos*, 5ª ed.; Embrapa Solos: Brasília, 2018.
12. Silva-Filho, E. V.; Sella, S. M.; Spinola, E. C.; Santos, I. R.; Machado, W.; Lacerda, L. D.; *Microchem. J.* **2006**, *82*, 196. [Crossref]
13. de Paula, F. C. F.; Lacerda, L. D.; Marins, R.; Aguiar, J.; Ovalle, A.; Falcão Filho, C.; *Quim. Nova* **2010**, *33*, 70. [Link] accessed in April 2023
14. Lacerda, L. D.; *Braz. J. Aquat. Sci. Technol.* **2006**, *10*, 13. [Link] accessed in April 2023
15. Bouwman, A. F.; Lee, D. S.; Asman, W. A. H.; Dentener, F. J.; Hoek, K.W.; Van Der Olivier, J. G. J.; *Global Biogeochem. Cycles* **1997**, *11*, 561. [Crossref]
16. Malavoltas, E.; Dantas, J. In *Melhoramento e Produção do Milho no Brasil*; Paterniari, E., ed.; Fundação Cargill: São Paulo, 1980, p. 429.
17. Bidone, E. D.; Lacerda, L. D. In *A Preliminary Approach of the Link Between Socio-Economic and Natural Indicators into a Driver-Pressure-Impact-Response Framework Case Study: Guanabara Bay Basin, Rio de Janeiro, Brazil, LOICZ Reports & Studies 21*; Lacerda, L. D.; Kremer, H. H.; Kjerfve, B.; Solomons, W.; Marshall-Crossland, J. I.; Crossland, J. C., eds.; LOICZ: Textel, 2002, p. 142.
18. Bidone, E. D. In *Análise Econômica-Ambiental Aplicada à Contaminação de Águas Fluviais de Pequenas Bacias Costeiras do Estado do Rio de Janeiro*; Esteves, F. A.; Lacerda, L. D., eds.; Ed. UFRJ: Rio de Janeiro, 2000, p. 371-394.
19. Gianessi, L. P.; Peskin, H. M.; *An Overview of the RFF Environmental Data Inventory: Methods, Sources and Preliminary Results*, 1st ed.; Resources for the Future: Washington, 1984.
20. SanDiego-McGlone, M.; Smith, S. V.; Nicolas, V.; *Mar. Pollut. Bull.* **2000**, *40*, 325. [Crossref]

21. Varona, H. L.; Noriega, C.; Araujo, M.; *mStatGraph version 1.0*, Zenodo, Switzerland, 2021.
22. Greeland, D. J.; Lal, R.; *Soil Conservation and Management in the Humid Tropics*, 1st ed.; Wiley: Chichester, 1977.
23. Howarth, R. W.; Billen, D.; Swaney, A.; Townsed, N.; Janarski, K.; Lajtha, K.; Downing, J. A.; Elmgren, R.; Caraco, N.; Jordan, T.; Berendse, F.; Freney, J.; Kudeyorov, V.; Murdcoh, P.; Liang, Z. Z.; *Biogeochemistry* **1996**, *35*, 75. [Crossref]
24. Lacerda, L. D.; Molisani, M. M.; Sena, D. L.; Maia, L. P.; *Environ. Monit. Assess.* **2008**, *141*, 149. [Crossref]
25. Vasconcelos, V. H. F.: *Emissões Naturais e Antrópicas de Nitrogênio e Fósforo para os Principais Açudes da Bacia Hidrográfica do Rio Seridó, RN*; Dissertação de Mestrado, Universidade Federal do Rio Grande do Norte, Natal, Brasil, 2011. [Link] accessed in May 2023