Braz. J. Aquat. Sci. Technol., 2015, 19(2).

LAND USE EFFECTS ON NUTRIENT CONCENTRATION IN A SMALL WATERSHED IN NORTHEAST BRAZIL

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ABSTRACT

Silva, D.M.L.; Souza, M.F.L; Silva, F.S.; Paula, F.C.F.; Moraes, M.E.B. & Strenzel, G.M.R. (2015). Land use effects on nutrient concentration in a small watershed in northeast Brazil. Braz. J. Aquat. Sci. Technol. 19(2). eISSN 1983-9057. DOI: 10.14210/bjast.v19n2. Increases of N and P discharges from inland waters to coastal environments are the by-products of anthropogenic activities such as agricultural practices and urbanization. Therefore, the aim of this work was to evaluate the influence of land use change in nutrient concentrations in a small watershed in southern Bahia, Brazil. The study sites were characterized by secondary forest with different regeneration stages, deforested areas, crops, urban area and mangrove. Dissolved forms of both nitrogen and phosphorus were higher than particulate forms in all sites. The dissolved organic nitrogen (DON) concentration was higher than the dissolved inorganic nitrogen (DIN) and the concentration of DON made up 60-73% of the total dissolved nitrogen (TDN). Seasonally, it was not observed variations between dry and rainy season in nutrient concentrations in Cururupe River Basin, with the exception of DON, which was higher in the rainy season. DIN, DON, particulate organic nitrogen (PON) and dissolved silica (DSi) export varies over the hydrological year indicating that fluxes were correlated with discharge. In addition these particulate forms and total suspended sediment were positively correlated with deforested area. Even though most of area of the Cururupe River Basin is occupied by secondary forests, the conversion to different land uses presented low alterations in water quality.

Key words: Nutrients, Stream, Land use.

INTRODUCTION

Rivers and streams acts as integrators of land-water interactions. Small watersheds are good indicators of the structure and functioning of the aquatic ecosystems due to the high sensitivity related to the changes observed in their environment. In this context, small watersheds play an important role in the biogeochemical cycles of several elements, including nitrogen (N), carbon (C), phosphorus (P) and, oxygen (O) (Galloway et al., 2003, 2008; Likens et al., 2004). In addition to the fact that nutrients are essential for life, in high concentration, they can act as contaminants in water (Sprague & Lorenzen, 2009). In recent decades, freshwater and coastal eutrophication has increased, leading to a loss of biodiversity, environmental degradation, alteration of food web structure, taste and odor problems, and increase of algal blooms (Dodds et al., 2008, 2006; Falkwolski et al., 2000; Gravelle et al., 2009; Howarth, 2008, Lombardo et al., 2010). Two key nutrients, nitrogen (N) and phosphorus (P) are the main agents responsible for this process. Streams and rivers can contribute with a high load of nutrients to coastal areas and oceans. Before reaching the ocean, nutrients from terrestrial ecosystems that reach inland waters can undergo biological and physicochemical processes and they can be immobilized or transformed and transported to estuaries and consequently ocean areas (Conley et al., 2000). Nutrients transported from rivers to oceans have received attention of researchers since these anthropogenic alterations have modified several of these ecosystems.

Land use change is one of the major anthropogenic influences on aquatic systems, which affects the water quality of rivers (Zhou et al., 2012). Increases of N and P discharges from inland waters to coastal environments are the by-products of human activities such as agricultural practices (use of fertilizer in crops and pastures) and mining of phosphate rocks such as apatite and emission of urban and domestic effluents such as detergents and sewage (Marins et al., 2007; Ortiz-Zayas et al., 2006; Pellerin et al., 2004; Silva et al., 2007).

Strong positive relationships have been observed between agriculture and urbanization and water nutrient concentrations. Agricultural watersheds represent a mosaic of intensively and extensively managed lands being the major source of suspended solids and inorganic nutrients (phosphates and nitrates) to rivers ans streams (Mendiguchıa et al., 2007)

Forest clearing for farms and pastures leads to an increase of overland flow (Germer et al., 2009, Michaud & Wieger, 2011) and several solutes such as phosphates, nitrate, calcium, magnesium, etc. Finally, nutrient concentration may be also affected by municipal sewage effluents that increases the eutrophication processes.

Nutrient inputs in freshwater chemistry have been modified in the last three decades and a lack of information about the trophic state of these environments has been reported, mainly in tropical ecosystems (Lombardo et al., 2010). Due to this importance in maintaining several processes, disturbance in these element cycles can promote alterations in the structure and functioning of terrestrial and aquatic ecosystems and studies about these nutrients in these ecosystems have been essential to estimate the relative importance of the inputs of C, N and P from atmosphere and rock weathering (Dodds, 2006)

Due to the fact that N is essential for life, this element limits primary productivity in several ecosystems (Vitousek & Howarth, 1991). Nitrogen on earth is found mainly in the molecular form, and mostly found in the atmosphere and is naturally available for terrestrial ecosystems through biological fixation, wet and dry deposition and lightning. Most nitrogen delivered to freshwater ecosystems comes from land through runoff and lixiviation, due to this, changes in land use are important factors that could alter the nutrient concentration in small watersheds. The main natural phosphorus source is weathering of rocks and inorganic P results from microbial decomposition. On the other hand, P concentrations show different responses to anthropogenic sources coming from different pathways and sources (Gravelle et al., 2009). The main sources of P have been deposition (wet and dry), soil and agronomic inputs (fertilizers, plant residue and animal feces) and industrial and domestic sewage (Zaimes& Schultz, 2002).

The main source of dissolved silica (DSi) is soil leaching and erosion resulting from continental weathering and breakdown of minerals (Conley et al., 2000; Kolszilnik & Tomaszek, 2008). The DSi is taken up by macrophytes and siliceous phytoplankton, such as diatoms, and this leads to a depletion of this element in the aquatic ecosystems (Kolszilnik & Tomaszek, 2008). It has long been known that anthropogenic activities affect the transport of N and P, however less information area reported about the production and transport of DSi (Conley et al., 2000). DSi concentrations have been altered by construction of dams that acts like a silicon trap leading to several consequences for food web (Conley et al., 2000, Humborg et al., 2000).

The relationship between land use changes and nutrient concentration in streams have been extensively studied in temperate and tropical systems (Germer et al., 2009; Gravelle et al., 2009; Silva et al., 2012; Evans et al., 2014; Halstead et al., 2014). Studies in Brazilian streams have been developed mainly in southern and north however few studies have been carried in northeast regions. Southern Bahia is considered one of the most important centers of cocoa production ("cabruca"), including cities such as Ilhéus and Itabuna that have around 200,000 inhabitants, respectively, and present several types of agricultural activities. Therefore, the purpose of this work is to evaluate the influence of land use change in nutrient concentrations in a small watershed in southern Bahia Brazil.

SAMPLING AND METHODS

Site description

The Cururupe River Basin located in the State of Bahia, Brazil has an approximate area of 88,96 km2 presenting several types of land use change. Most of the watershed is covered by secondary forest (81.8%) followed by deforested area (12.0%), crops such as cocoa, banana (3.2%), bare soils (1.3%), small dams (0.24%) and shrubs (0.1%). Urban (0.98%) and mangrove areas (0.38%) are located exclusively at site 5 that represents a estuarine area. The geologic setting is composed of unconsolidated siliciclastic sediment of the Barreiras Formation. The climate is warm and wet (Af in Koppen classification) without a well-defined dry period with annual precipitation around 2200 mm yr^{-1}.

Land use mapping was based on the interpretation and scanning screen of a composite RGB satelliteIkonos.2005 with a 1-meter resolution, which was based on a geo-referenced topographic IBGE (Instituto Brasileiro de Geografia e Estatística). The Geographic Information System IDRISI Andes and the program Cartalinx version 1.2 were used (Clark Labs). A subwatershed (drainage area) was delineated for each of the five sites and the percentages were calculated for land use (Table 1 and Figure 1).

Table 1: Land cover percentages at Cururupe River Basin in northeast Brazil

	LAND USE								
Sites	**Coordinates**	**SECONDARY FOREST**	**URBAN**	**BARE SOIL**	**DEFORESTED**	**MANGROVE**	**CROPS**	**DAM**	**SHRUBS**
1	14°57'53.7'' 39°2'3.84''	89.32	0.00	1.07	0.01	0.00	9.60	0.00	0.00
2	14°55'21.9'' 39°2'22.7''	89.79	0.00	0.58	4.88	0.00	4.33	0.43	0.00
3	14°54'42.5'' 39°4'40.6''	80.75	0.00	1.26	15.87	0.00	2.06	0.05	0.00
4	14°52'56.5'' 39°2'22.5''	83.50	0.00	0.32	10.20	0.00	5.12	0.50	0.36
5	14°52'55.4'' 39°1'27.6''	72.92	5.30	3.02	16.08	2.04	0.32	0.22	0.11

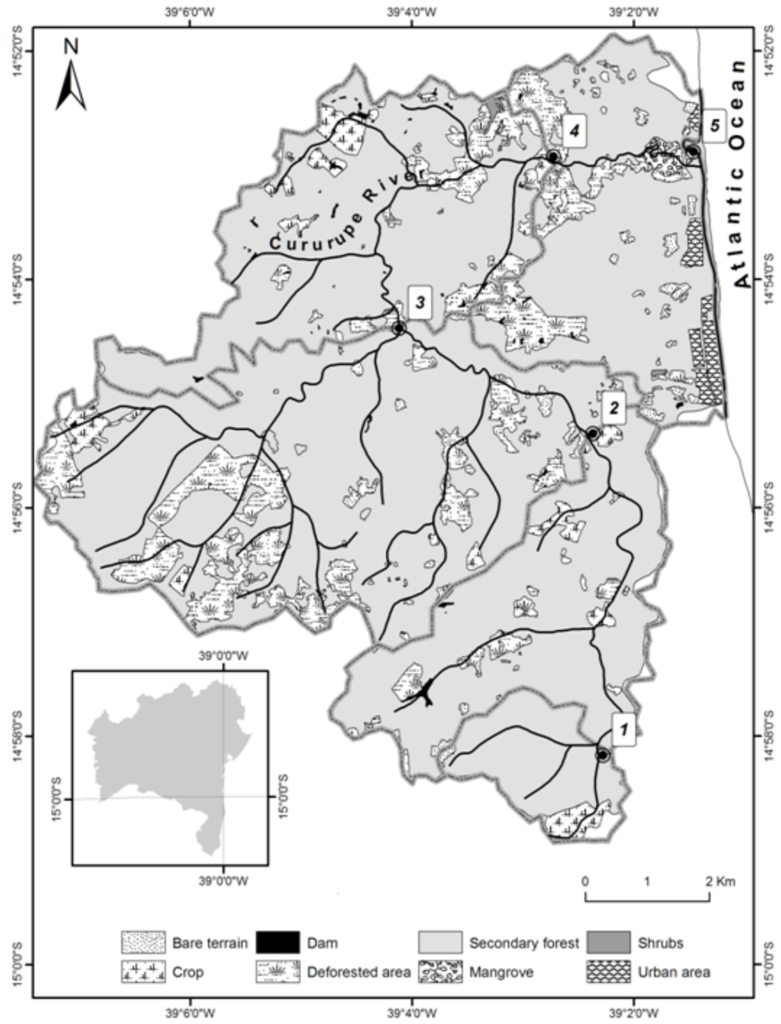

Figure 1 – Study area showing sampling sites and land use in of the Cururupe River Basin in northeast Brazil.

Field and laboratory methods

Water samples were collected monthly in five site collects from March 2007 to September 2008 (n=15). All flasks were cleaned with 1:1 HCl solution distillate water before use. Abiotic parameters (pH conductivity, dissolved oxygen and temperature were measured in the field with portable digital meters (WTW 5490). Water samples were filtered through a glass filter fiber (0.7 µm nominal pore diameter) pre combusted over 450 oC for 3 hours and stored in polyethylene flasks until laboratory analyses. Total suspended solids were measured in the glass filter fiber by gravimetric method (Strickland and Parsons. 1998). Dissolved inorganic nitrogen (DIN) and phosphorus (NO^{3-}.NO^{2-}.NH^{4+}. PO_4^{3-}) were analyzed in ion chromatography (DIONEX ICS1000) (USEPA 300.1 Method). Ammonium was separated in a CG12A/ CS12A column and sulfuric acid as eluent (15mM). Nitrite and nitrate were separated with AG9-HC / AS9-HC column with Carbonic Sodium as eluent (9mM). Both of them were prepared with ultra pure water (18MΩ.cm). Dissolved silica (DSi) was analyzed by spectrophotometric method according to Grasshoff et al. (1983). Total Dissolved Nitrogen (TDN) and Total Dissolved Phosphorus (TDP) were measured with persulfate digestion and analyzed by spectrophotometric method (Grasshoff et al., 1983). Particulate nitrogen and phosphorus were measured in the glass filter fiber by the same method used for TDN and TDP. The concentration of DON (Dissolved Organic Nitrogen) was calculated by the difference between TDN and DIN (Dissolved Inorganic Nitrogen) and PON was calculated by the difference between TDP and PO_4^{3-}. Chlorophyll-a analysis was performed following Parsons (1984) through acetone 90% extraction. The flux of dissolved inorganic nutrients was obtained by multiplying concentration values at site 4 by the calculated monthly fluvial discharge. To determine the stream discharge it was used a hydrologic model calculation, rainfall-runoff - which uses temperature, monthly rainfall, watershed area and percentage of watershed unmeasured. This model was based on Smith et al. (1999) according the Schreiber equation:

$$Q = A * \left(\frac{Af}{r}\right) * \left(\frac{r}{2.74} * Di * 10^6\right)$$

where:

A = watershed area
Af = monthly runoff
Di = number of days in the ith month
r = precipitation
Q = monthly fluvial discharge

The flux of dissolved inorganic nutrients was obtained by multiplying concentration values at site P4 by the calculated monthly fluvial discharge (Q). Fluxes were normalized dividing them by the area of drainage basin according the equation:

where:

$$Fny = \frac{Fy}{Ast}$$

Fny = normalized flow of dissolved nutrients
Fy = actual flow of nutrient in P4
Ast = drainage area of P4

Statistical analyses

The Kolmogorov-Smirnov and Lilliefors test was used to test the normality distribution. If the values did not have a normal distribution, a Kruskall Wallis test ($p<0.05$) was applied to test for statistically significant differences between collection sites. To test temporal variation, a non parametric U Mann Whitney t-test to determine whether there is a significant difference between the dry (June, August/2007, January, February, April, May, July and September/2008) and rainy season (March, April, May, September, October, November, December/2007, March/2008). The Pearson's product moment correlation coefficient, r, was used to assess the relationship between land use and water chemistry variables.

RESULTS

Abiotic parameters are presented in Table 2. The annual means of pH were significantly lower in site 1 and 2 ($p<0.05$) and ranged from 4.6 to 7.0 with the higher values found in site 5. Conductivity was also higher in site 5 with values ranging from 361-8660 µS cm-1 ($p<0.05$). Dissolved oxygen ranged from 5.5 in site 5 to 6.5 mg L-1 in site 1 however it was not observed statistical differences between the collection sites.

Nitrate was the main dissolved inorganic nitrogen (DIN) form presented in most of all sites followed by ammonium and nitrite, which, was below the detec-

Table 2: Annual mean concentration of abiotic parameters and nutrients at Cururupe River Basin in northeast Brazil (mean ± sd).

n=16	*1*	*2*	*3*	*4*	*5*
pH	4.6 ± 0.4	5.6 ± 0.3	6.9 ± 0.5	6.9 ± 0.3	7.0 ± 0.4
Conductivity	45.5 ± 3.8	43.9 ± 2.7	49.6 ± 2.2	47.5 ± 2.0	5311 ± 2649
Dissolved oxygen	6.5 ± 0.9	6.0 ± 1.4	6.3 ± 0.7	6.3 ± 0.8	5.5 ±1.0
N - NO_3^-	3.4 ± 1.7	3.1 ± 2.3	4.3 ± 1.3	4.8 ± 0.7	3.5 ± 1.4
N- NH_4^+	3.5 ± 2.8	2.4 ± 1.7	2.6 ± 1.1	3.8 ± 2.5	<l.d.
N- NO_2^-	0.23 ± 0.73	0.03 ± 0.1	0.03 ± 0.1	0.02 ± 0.06	<l.d.
P - PO_4^{3-}	0.5 ± 1.5	0.2 ± 0.6	0.3 ± 0.8	0.1 ± 0.4	<l.d.
DSi	8.7 ± 6.2	3.8 ± 4.5	16.1 ± 11.9	15.2 ± 20.4	56.3 ± 28.3
PON	0.2 ± 0.1	0.3 ± 0.2	0.6 ± 0.4	0.4 ± 0.2	0.5 ± 0.2
DON	18.5 ± 13.0	16.6 ± 10.5	13.3 ± 12.8	13.6 ± 11.4	20.7± 8.0
POP	0.1 ± 0.03	0.1 ± 0.05	0.13 ± 0.06	0.2 ± 0.12	0.2 ± 0.1
DOP	0.4 ± 0.5	1.0 ± 0.7	0.8 ± 0.4	1.1 ± 1.1	0.9 ± 0.6
TSS	2.8 ± 4.4	4.3 ± 4.9	8.9 ± 10.7	9.4 ± 10.4	11.6 ± 4.8
chl-a	1.7 ± 0.8	5.9 ± 3.0	10.2 ± 5.1	9.1 ± 5.1	6.8 ± 5.2

Conductivity (µS cm $^{-1}$). Dissolved oxygen (mgL^{-1}). Nutrients (µM). TSS (mgL^{-1}). chl-a (µg L^{-1}). <l.d.-above the detection limits ($LD_{PO4}{}^{3-}$=0.008µM e $LQ_{PO4}{}^{3-}$ = 0.08µM and $LD_{NO2}{}^{-}$=0.02 µM and LQ_{NO2} = 0.15µM).

tion limits in site 5 (<0.02 µM) (Table 2). The nitrate concentration range from 3.1 to 4.8 µM to site 1 and 4, respectively. Phosphate was lower than detection limits for almost all samples (high standard deviation). In the site 5 it was not possible to quantify this parameter (<0.008 µM). There is no significative differences in phosphate concentration between dry and rainy season and this ion presents a slightly decrease upstream to downstreams ranging from 0.5 to 0.1 µM from site 1 to 4 (Figure 2). Silicate concentration presented no changes along the basin, but occurred in higher concentration in the estuarine area (site 5) (mean annual of 56.3 µM – $p<0.05$).

Dissolved forms of both nitrogen and phosphorus were higher than particulate forms in all sites. The DON concentration was higher than the DIN in all collection sites (Table 2). The highest concentration of DON was found in site 5 followed by site 1, 2, 4 and 3 and made up 60-73% of the total TDN. Temporal variation showed slight differences between the dry and rainy season; however, significant differences ($p<0.05$) were observed for DON in site 4 and 5 and the particulate forms of phosphorus and nitrogen to site 1 and 3, respectively (figure 2).

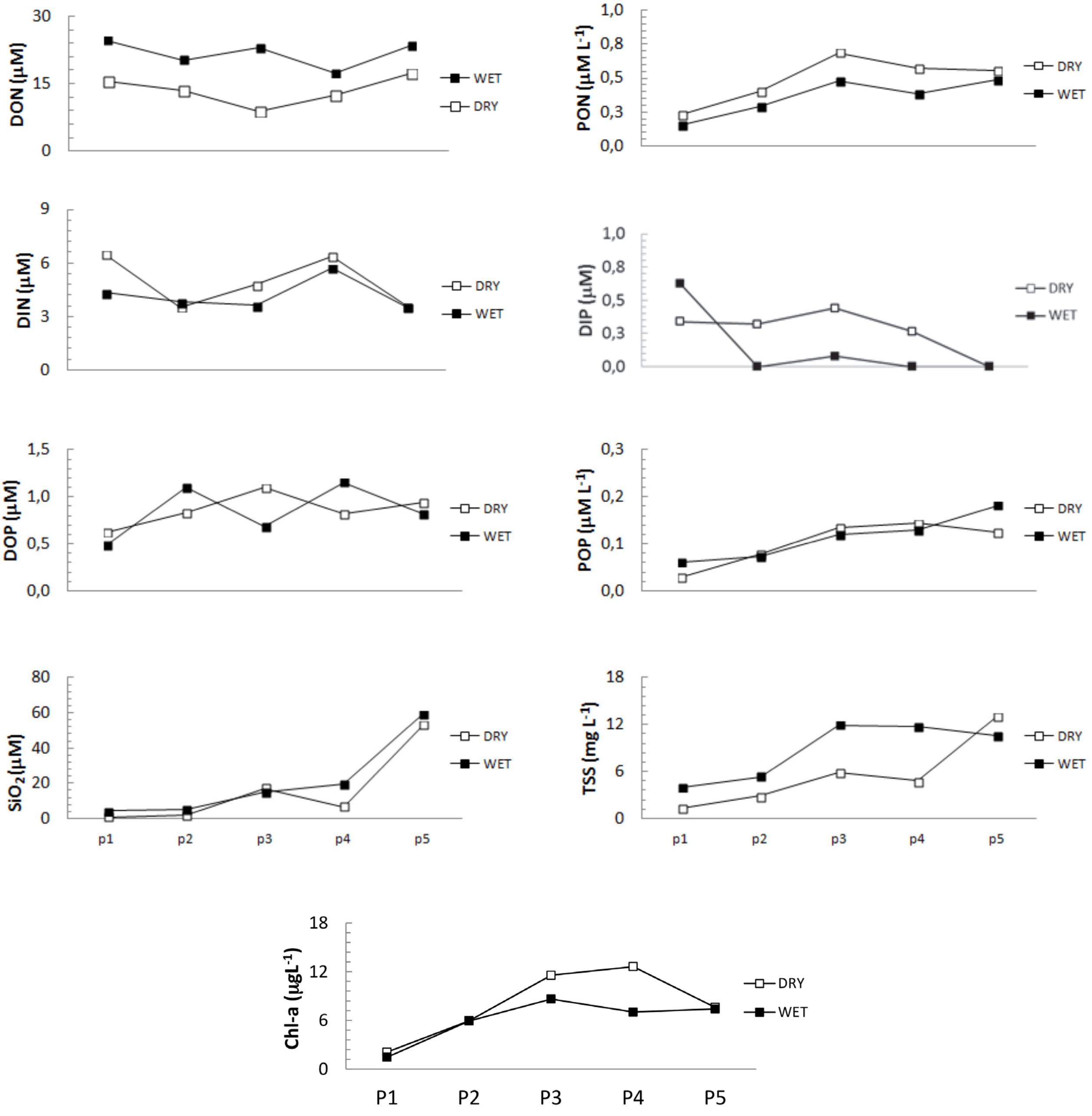

Figure 2 – Seasonal variation (dry and wet season) of nitrogen and phosphorus (µM) chlorophyll-a (µg L^{-1}) and total of suspended solids (mg L^{-1} - TSS) at Cururupe River Basin in northeast Brazil.

Particulate forms of nitrogen and phosphorus were strongly correlated positively with land use changes, mainly deforested areas (0.98 and 0.97, respectively). TSS showed similar pattern presenting significant positive association with deforested areas and negatively with secondary forest (-0.92 and 0.93, respectively). In addition, as showed above, DSi seems to be correlated positively with mangrove, urban areas that are exclusively located at estuarine site and negatively with secondary forest (Table 2 and 3).

The monthly export of total nitrogen and phosphorus are presented in Figure 3. DIN, DON, PON and DSi export varies over the hydrological year indicating that fluxes were correlated positively with discharge (Pearson= 0.73, 0.84, 0.55 and 0.65 respectively). Dissolved and particulate phosphorus did not present strong correlation with discharge.

Chl-a present significant differences from upstream to downstream with the higher concentrations observed in site 3 and 4 compared to site 1 ($p<0.05$) but no differences between dry and rainy season (figure 2). Despite the increase of chl-a, it was not observed correlation with the land use change. Chl-a showed the lower coefficient correlation of all parameters analyzed (Table 3).

Table 3: Correlations between land use (%) and water chemistry at Cururupe River Basin northeast Brazil.

	Urban	Bare soil	Secondary Forest	Deforested	Mangrove	Crops	Dam	Shrubs
pH	0.42	0.33	-0.79	**0.95**	0.42	-0.85	0.32	0.51
Conductivity	**1.00**	**0.94**	-0.83	0.53	**1.00**	-0.63	-0.05	0.07
Dissolved oxygen	0.86	0.64	-0.77	0.59	0.86	-0.70	0.45	0.47
OD	-0.88	-0.69	0.64	-0.44	-0.88	0.67	-0.39	-0.19
N - NO_3^-	-0.21	-0.31	-0.24	0.38	-0.21	-0.06	0.30	0.81
N- NH_4^+	**-0.92**	**-0.91**	0.76	-0.58	**-0.92**	0.77	0.09	0.21
N- NO_2^-	-0.35	-0.18	0.56	-0.77	-0.35	0.87	-0.62	-0.39
P - PO_4^{3-}	-0.64	-0.41	0.67	-0.69	-0.64	0.83	-0.63	-0.46
SiO_4	**0.96**	**0.90**	**-0.96**	0.74	**0.96**	-0.76	-0.01	0.21
PON	0.37	0.36	-0.78	**0.98**	0.37	**-0.89**	0.16	0.30
DON	0.66	0.57	-0.16	-0.28	0.66	0.09	-0.04	-0.08
POP	0.52	0.46	**-0.88**	**0.97**	0.52	-0.86	0.19	0.46
DOP	-0.01	-0.20	-0.25	0.58	-0.01	-0.65	0.73	0.43
TSS	0.64	0.54	**-0.92**	**0.93**	0.64	-0.82	0.21	0.52
chl-a	-0.03	-0.04	-0.47	0.82	-0.03	-0.69	0.26	0.33

*Correlations with $p < 0.05$ are in bold

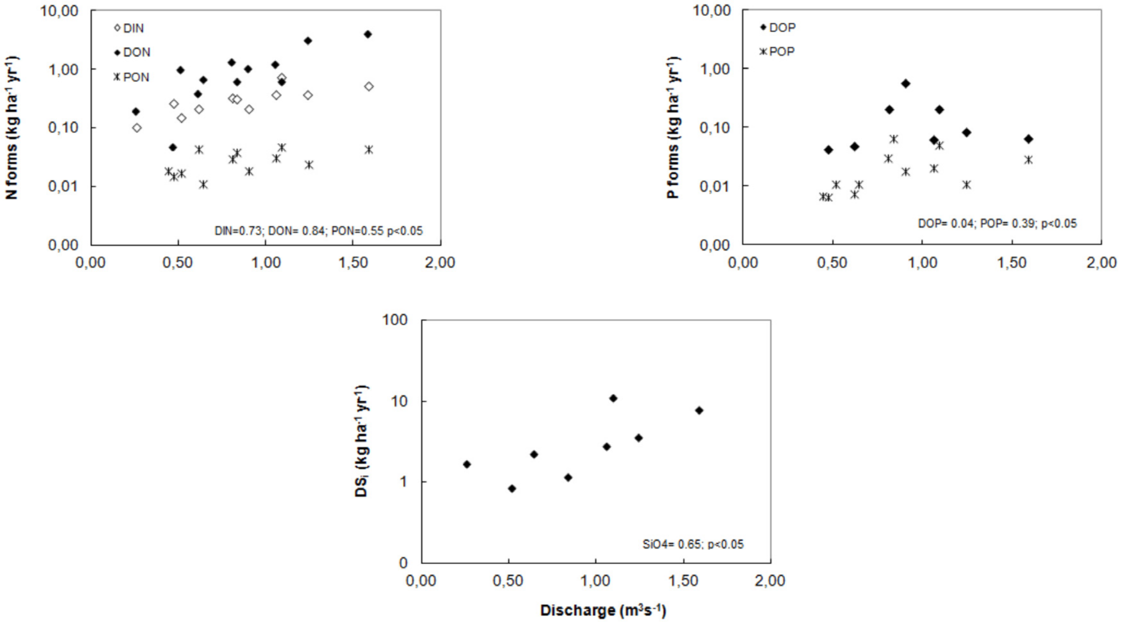

Figure 3 – Correlation between N. P and DSi export (kg ha^{-1} yr^{-1}) and discharge (m^3 s^{-1}) at Cururupe River Basin in northeast Brazil.

DISCUSSION

Several studies have shown that land use alters the biogeochemical cycles of small watersheds. Anthropogenic activities can alter the nutrient export to streams and urbanization and agricultural practices are responsible for the main alterations in the water geochemistry (Deegan et al., 2001; Gravelle et al., 2009; Krusche et al., 1997; Silva et al., 2007; 2012). Our study suggests that due to the fact that almost all basin is covered by secondary forest with different regeneration levels, it was not found large differences among site collects.

The distribution of N and P forms in small tropical watersheds has been well studied in recent decades (Andrade et al., 2011; Asbury & McDowell, 1994; Biggs et al., 2004; Neill et al., 2001; Parron et al., 2011; Silva et al., 2007). In the present study, the main dissolved N form exported in the Cururupe River Basin was DON, followed by inorganic and particulate forms (figure 2 and 3). This behavior has been observed in undisturbed watersheds in tropical ecosystems that present weak N retention (Andrade et al., 2011; Downing et al., 1999; Parron et al., 2011; Silva et al., 2012). Watersheds located in coastal areas in Bahia state (Silva LP unpublished data) and in the Amazon (Neill et al., 2001) presented dissolved organic N as the main exported element. These studies showed that 50 to 60% of exported nitrogen was in organic form showing that DON presents high mobility through soil and soil solutions (Chaves et al., 2009; Neill et al., 2001). Similar patterns were also observed in Cerrado watersheds by Parron et al. (2011); however, the lower N and P output from stream water compared to inputs (precipitation and throughfall) showed a conservative N cycling in this ecosystem.

Although DON did not show differences between sites, nitrate showed a slight increase from site 1 to 4. The increase of inorganic N in disturbed watersheds has been described for several regions. Small watersheds with different land uses, such as silviculture and sugar cane, in São Paulo state, showed an increase of 20 µM of nitrate after the river extended across these areas (Silva et al., 2007). Significant increases of NO^{3-}, NH^{4+} and NO^{2-} from natural to urban areas were also found in streams in central Brazil demonstrating that land use changes the stream chemistry (Silva et al., 2012).

Despite the presence of alterations due to land use changes in the Cururupe River Basin, small watersheds in southern Bahia present low nutrient concentrations compared to other regions in Brazil. Streams in the Atlantic forest in southeast Brazil presented higher NO^{3-} values compared to our study. Nitrate in pristine areas in coastal streams in Ombrophilus dense forests ranged from 11 to 14 µM in Ubatuba (Andrade et al., 2011) and from 20 to 24 µM in the Ribeira de Iguape watershed (Silva et al., 2012). In our study these values did not exceed 5 µM. On the other hand, our results coincide with streams located in pristine areas in Ombrophilus dense forests in the Amazon (Neill et al., 2001), the Cerrado in central and southeastern Brazil (Parron et al., 2011; Silva et al., 2012) and Semi-deciduous forest in southeastern Brazil (Silva et al., 2012). The main causes of these differences are probably related to soil characteristics. Coastal areas in the Ubatuba and Ribeira de Iguape area are characterized by Cambisoils presenting higher mineralization and nitrification rates and a higher clay percentage, while in the other areas, the soil is characterized by Latosoils, which are acidic, chemically poor and dystrophic soils. According to Parron et al. (2011), areas characterized by these soil types present conservative mechanisms for maintaining ecosystem productivity with low hydrological outputs.

The same trend was observed in a small watershed in the Mangue River in southern Bahia with lower increases in N and P concentrations from upstream to downstream (Silva, DML unpublished data). As in the Cururupe River, this watershed presents different kinds of land use such as small crop cultivation and low urbanization. This fact could also be due to the soil properties that present 70 to 80% sand and a low mineralization and nitrification process and due to the geological formation. In these areas, the main geological formation is “Tabuleiros Costeiros”, which present lower nutrient concentrations (lower C/N DML Silva, unpublished data) and a high runoff process. In addition to, the lower exportation of NO3- in this watershed, as well as in watersheds under latosoils, suggests that biotic demand is high relative to supplies.

The lower DIP concentrations found in Cururupe River basin compared to nitrogen is due to the fact that this element is less mobile than nitrogen in soil, because it is absorbed in soil particles. At the same time, tropical soils are usually impoverished in P because the high concentration of iron that decreases its availability (Vitousek, 1984). Similar results were found in streams located in the Cerrado in central Brazil, which present weathered soils with a high concentration of iron which reduces the export to streams (Resende et al., 2011).

In addition, despite the fact that the Cururupe River Basin presented several alterations throughout the watershed, this basin still presents a high percentage of forested areas (secondary forest) that can also have an important influence on lower spatial variations in N and P biogeochemistry.

DIP presented low concentrations in all sites and at site 5 this form was lower than the detection limits in all months. This behavior is probably due to the increase assimilation by primary producers, since at this point (5), higher concentrations of DSi were found, as well chlorophyll-a concentrations were high (~ 7 µg . L^{-1}). Alves & Souza (2005) also observed DIP lower than the detection limit in samples at P5, but with chl-a values lower than 2 µg . L^{-1}. These authors suggested that phosphate ions could also be removed by adsorption to ferric oxyhydroxides suggesting a P limitation to the primary production at this point.

The higher silicate concentration at the estuarine station (5) than at the upper reaches of the basin was an unusual finding. High concentrations of silicate were already observed at this station by Alves & Souza (2005). Rivers are the higher concentration end member with respect to silicate estuarine mixing. Diatoms are the main primary producers of the coastal phytoplankton, and during the rainy season blooms are frequently observed at the beaches. The transport of these diatoms to the estuary during high tide, deposition at the sediment, and recycling of the siliceous frustules could explain the observed concentrations. DSi exported from rivers to ocean are influenced by weathering intensity, climatic variation and geology associated to presence of diatoms. Despite the fact that DSi was positively correlated with urbanization, it is not been recorded that DSi is influenced by anthropogenic activities. Little is known about correlation between DSi and land use changes, such as agriculture and DSi and eutrophication process. Eutrophication in rivers could alter the phytoplankton composition, and consequently diatoms frequency, due to an increase of turbidity and consequent decreased of photosynthetic process (Humborg et al., 2000). In our study urban area appears only in site 5 and DSi presented the higher values at this site, these factors could explain the good correlation found with this variable.

In addition, it can be observed that chl–a and TSS are inversely correlated with the dry and rainy season, with high TSS and lower chl-a in dry season and lower TSS and higher chl-a in rainy season which could be related to the decrease of incident solar radiation reducing algal proliferation. An increase of chl-a from upstream to downstream was also observed with the higher concentration found in site 3 and site 4 that presents significant differences with site 1 ($p<0.05$). Chl-a and TP are two extremely important parameters in algal biomass in aquatic systems (Araujo et al., 2008; Brandini et al., 2007;Calijuri et al., 2008, Kruger et al., 2006). Some factors may have contributed to this increase: first P3 and P4 are unprotected reaches covered by pasture and small crops. These land covers increase solar incidence on surface waters leading to the increase of photosynthetic process. At the same time these practices increases the N and P inputs through the runoff processes, which increase erosion, consequently increasing P sources.

Although particulate organic phosphorus (POP) and particulate organic nitrogen (PON) presented lower concentration, they presented, associated with TSS, a positively correlation with deforested area confirming that probably the erosion in the terrestrial environment is the main source of particulate nutrients in the watershed. Erosion increases following deforestation, which leads to a decrease of infiltration increasing the surface runoff (Bruijinzeel, 1991).

High inputs of nutrients have been associated with an increase in the rainy season (Chen et al., 2012; Jiang et al., 2012), which is more pronounced in areas with agricultural practices or urbanization. Seasonally, it was not observed variations between dry and rainy season in nutrient concentrations in Cururupe River Basin, with the exception of DON, which was higher in the rainy season for all sites ($p<0.05$). In addition, DON fluxes presented a strong correlation ($r=0.84$) with elevated fluxes observed with higher discharges. DON concentrations also showed seasonal differences in streams under pasture and forest in the Amazon region (Neill et al., 2001) and in streams in the Atlantic forest in southern Bahia (Silva, LP unpublished data). Losses of DON have been attributed to hydrological variations due to the association of this form with humic soil substances and consequent leaching with the increase of flow paths throughout these soils (Hedin et al., 1995).

CONCLUSION

Even though the primary vegetation of Cururupe River Basin was converted to different land uses, the water quality presented low alterations from upstream to downstream. The small number of studies in northeast Brazil makes it difficult to determine the main factors contributing to long-term effects of land use changes in small watersheds. However, removal of riparian vegetation would tend to contribute to higher nutrient export to streams promoting changes in N and P cycles.

ACKNOWLEDGEMENTS

We wish to thank FAPESP – Fundação de Amparo a Pesquisa do Estado da Bahia, CNPq (TO n° 0116/2005) and Universidade Estadual de Santa Cruz (PROPP n°00220.1300.574) for financial support. We are grateful to CTRAN/UESC for field assistances and we would like to thank Jim Hesson for the English revision of this manuscript

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Submetido: Março/2015
Revisado: Setembro/2015
Aceito: Outubro/2015