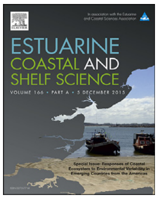
Estuarine, Coastal and Shelf Science 166 (2015) 34–44

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss



Natural and anthropogenic emissions of N and P to the Parnaíba River Delta in NE Brazil

Francisco José de Paula Filho [a, *], Rozane Valente Marins [b], Luiz Drude de Lacerda [b]

[a] Universidade Federal do Piauí, Campus Profª Cinobelina Elvas, Rod.BR 135, Km 03, sn, Planalto Horizonte, 64.900-000, Bom Jesus, PI, Brazil
[b] Universidade Federal do Ceará, Instituto de Ciências do Mar/LABOMAR, Av.da Abolição, 3207, 60.165-081, Fortaleza, CE, Brazil

ARTICLE INFO

Article history:
Accepted 13 March 2015
Available online 24 March 2015

Keywords:
nitrogen
phosphorus
watershed
nutrient transport
meso-active
eury-active

ABSTRACT

The Parnaiba River Delta is the largest open sea delta in the Americas, having a unique ecological importance for the conservation of wildlife and fisheries resources. However, little is known about the biogeochemistry of this ecosystem. This study estimates N and P emissions to the delta using emissions factors, calibrated with field samples and N and P concentrations in different compartments of the delta. The estimated loads totaled 14.517 t N year^{-1} and 8.748 t P year^{-1}, indicating that anthropogenic N and P emissions outweigh natural emissions by approximately 5 and 10 times, respectively. The activities that contribute the most to this result are livestock farming, agriculture and the release of untreated domestic sewage. The flows of N and P from the estimated loads corresponded to 339 kg N km^{-2} year^{-1} and 204 kg P km^{-2} year^{-1}, so the region can be classified as “meso-active” and “eury-active” with regard to the transfer of nutrients. These results are consistent with the coastal megabasin design (COSCATs) proposed by Meyback et al. (2006). This article presents a first approach to the calculation of an estimated annual emissions inventory of N and P for the lower basin of the Parnaíba River and its coastal region, representing an approach that has been satisfactorily used in assessing the sensitivity of estuarine systems in northeastern Brazil.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The excessive, global and indiscriminate release of nutrients in water bodies affects basins at different scales. The felling of forests and their transformation into crop and pasture fields or urban expansions increase the emissions of phosphorus (P) and nitrogen (N) derived from human activities, which are finally deposited in lentic and lotic systems, wetlands, coastal waters and groundwater, modulating the trophic status of such water bodies (Seitzinger et al., 2005, 2010; Filoso et al., 2006; Meyback et al., 2006).

The relative contribution of nutrient intakes for an individual system is difficult to quantify because of the wide variety of sources in any given watershed. The direct measurement of N and P concentrations in the environment to calculate their flows is quite complex and costly. Therefore, environmental researchers and agencies have employed a strategy of estimating continental inputs of N and P to the oceans from river flows using empirical emission factor models (USGS, 2011). These models take into account data related to major nutrient sources within the basin, according to the types and uses of the soil, area and vegetal coverage of the basin, river flows, rainfall levels, fertilizer application, census data on the distribution of animal and human populations, and atmospheric deposition (EEA, 2000; USEPA, 2003; Lacerda et al., 2006; Noriega and Araujo, 2009), including pollutant sources, factors influencing terrestrial and aquatic transportation, and socioeconomic data on production and consumption at the local, regional and global levels. This has become a very effective tool for measuring the loads of nutrients exported by the rivers (Lacerda et al., 2008; Seitzinger et al., 2010; USGS, 2011).

An emission factor is a number that represents the amount of a contaminant released into a receiving body from an activity associated with that factor. It is a fundamental decision-making tool for the proper management of water resources and the development of strategies to control and mitigate impacts of different contaminants. This approach has been widely applied locally (Paula et al., 2010; Molisani et al., 2013), regionally (Howarth et al., 1996; Boyer et al., 2002; Filoso et al., 2006; Lacerda et al., 2006; Martinelli et al., 2010; USGS, 2011) and globally (Caraco and Cole,

---

* Corresponding author.
E-mail address: franciscojose@ufpi.edu.br (F.J. de Paula Filho).

http://dx.doi.org/10.1016/j.ecss.2015.03.020
0272-7714/© 2015 Elsevier Ltd. All rights reserved.

1999; Smil, 2000; Howarth et al., 2008; Seitzinger et al., 2010). Its application in the quantification of N and P in river basins is relatively simple, depends on the characteristics of the nutrient sources and requires considerably few input data. These models are validated through their calibration, using a set of local or regional data (i.e. basin area, sanitation, fertilizer application, rainfall, NO_3^-, NH_4^+ and PO_4^{3-} in water, soil loss, soil retention factor). Emission factors are a valuable tool for environmental managers for allowing visualize past trends and develop future scenarios of nutrient export by watershed (Seitzinger et al., 2010).

The increase of fish mortality episodes and excessive proliferation of aquatic weeds, the growth in the number of occurrences recorded in the healthcare system related to algal blooms and problems associated with cyanobacterial toxins are the consequence of excessive inputs of N and P to inland waters and coastal areas (Andersen et al., 2006; Paerl, 2009). These effects are particularly dramatic in areas with a notorious water deficit in northeastern Brazil, resulting in restrictions to food production and availability of water for human consumption (Vasconcelos et al., 2011; Barbosa et al., 2012). Studies in the drainage basins of the NE region of Brazil showed that anthropogenic emissions of N and P and some trace metals exceed natural emissions by at least one order of magnitude and that these additional loads can change the quality of estuarine waters (Lacerda et al., 2006; Noriega and Araujo, 2009; Cunha et al., 2010; Paula et al., 2010; Marins et al., 2011).

The inclusion of river basins of NE Brazil in the global scenario of continental flows to the oceans is difficult due to the lack of systematic in situ measurements of loads, flows and concentrations, a fact that can be reverted by the use of emission factors (Paula et al., 2010). On a regional scale, the drainage basins located in this region include areas highly sensitive to environmental impacts related to human activities. Therefore, it is essential to outline consistent indicators aiding in the rating of the environmental conditions of these basins (Lacerda et al., 2008).

This study aims to present and calibrate an inventory of major natural and anthropogenic sources of N and P and their loads released annually to the Parnaiba River Delta, located in the semiarid region of northeastern Brazil, using the emission factors approach. This is a starting model in an attempt to determine the flow of nutrients exported from the basin to an important area of the Brazilian coastline.

2. Methodology

2.1. Studied area

The lower basin of the Parnaiba River, situated in NE Brazil, has a drainage area of 42.810 km^2 and a length of 380 km, crossing the Savannas, Caatinga and Coastal Marine biomes (Fig. 1). It has a flow of 770 $m^3\ s^{-1}$, a hot and humid climate and a rainy season concentrated between February and May with an average of 1.152 mm yr^{-1}. It spills into the Atlantic Ocean through the only open sea delta in the Americas. It is characterized by extensive fluvial-marine plains and a micro-to meso-tidal regimen in its estuary (MMA, 2006). The Parnaiba River Delta system is a complex and important ecosystem, having its own river-marine dynamics and harboring important plant communities and animals. It has a wide coverage area of about 2.750 km^2, corresponding to 15% of mangrove vegetation (Mesquista and Barreto, 2011). This complex configuration of ecosystems environment transforms this into an important global conservation area (MMA, 2006). Due to its environmental importance, in 1996 the Delta was declared an Environmental Protection Area Extending over three states in Northeastern Brazil. The Parnaíba watershed is characterized by a low industrial development. The delta has few point sources of contaminants and therefore diffuse pollution sources prevail, which are typically difficult to control and monitor.

The basin includes 60 counties belonging to three states Ceará (CE), Piauí (PI) and Maranhão (MA), with an overall population of 1.323.250 inhabitants (IBGE, 2012). The main land uses are grasslands (10%), agricultural areas (8%), uncultivated forest areas (48%), conservation areas (16%), urban areas (1%) and others such as wetlands, water bodies, exposed soils, dunes and mangroves (17%). The main soil types are latosols (10.367 km^2), plinthosols (10.900 km^2), podzols (8.481 km^2), lithic soils (6.078 km^2), dystrophic (2.310 km^2) and marine (487 km^2) quartz sands, planosols (1.639 km^2), alluvial (1.439 km^2), solonchak (593 km^2), gleysols (134 km^2) and solonetz (130 km^2). The areas corresponding to mangroves, lithic soils, sands and sea cliffs were not considered in the inventory of soil sources since the mangroves are considered to be accumulation areas. The leaching in lithic soils occurs at a geological time scale and beaches and sea cliffs export materials directly to the sea (Paula et al., 2010). The main economic activities in this area are linked to agriculture and livestock farming, with greater emphasis on dry land agriculture (i.e. soy, rice, beans, corn, cashew, cotton and sugarcane), bovine, goat and shrimp farming. The secondary sector is not too significant, with an incipient participation of the sugar and alcohol agribusiness (CODEVASF, 2006). There is no sewage grid, resulting in the discharge of untreated domestic wastewater to the streambeds, rivers and lakes. Data on the region's water quality is scarce and there is no effective and continuous monitoring system to assess the water quality status in its water bodies (MMA, 2006; ANA, 2012).

2.2. Tools and data for the calculation of N and P flows

The following criteria were considered when choosing the emission factors to quantify the loads of N and P from natural and anthropogenic sources in the low Parnaiba River: (a) the relevance of the collected information for it to accurately reflect the most significant emissions in the system, aiming to reduce the uncertainties to the minimum; (b) the compilation of sufficiently comprehensive, meaningful and preferably regionalized data so as to maximize the reliability of the results; (c) ensure that the information is consistent and comparable over time. All 60 counties in the basin were considered for the purposes of the inventory. The qualitative and quantitative characteristics of natural and anthropogenic (socioeconomic) sources for the inflows and outflows of N and P are expressed by formulas representing each activity or process (see Equations (1)–(10)). In most cases, the emission factors used in this study were adapted according to local data available from governmental statistics sources (IBGE, 2012; SNSA, 2012; ANA, 2012).

2.2.1. Natural sources: atmospheric inputs and soil denudation

Since the larger the basin area the larger the atmospheric deposition, nutrient loads from this source are directly related to basin area and the concentration of the chemical species resulting from atmospheric deposition, adjusted by the retention rate of the element by the soil. N and P emissions associated to atmospheric deposition were estimated according to Equation (1) below.

$$\mathbb{L}_{A\ell}^{\boldsymbol{N},\boldsymbol{P}} = \boldsymbol{\rho}_{\mathscr{R}w} \cdot \boldsymbol{A}_{Ws} \cdot (1 - \boldsymbol{\alpha}_{\boldsymbol{r}S}) \Big/ 10^3 \tag{1}$$

Where $\mathbb{L}_{A\ell}^{\boldsymbol{N},\boldsymbol{P}}$ is the estimated N or P load from atmospheric deposition, $\boldsymbol{A}_{W_s}$ is the basin area (km^2) and $\boldsymbol{\rho}_{\mathscr{R}w}$ is the deposition of N and P depending on the nutrient concentration in rainwater and

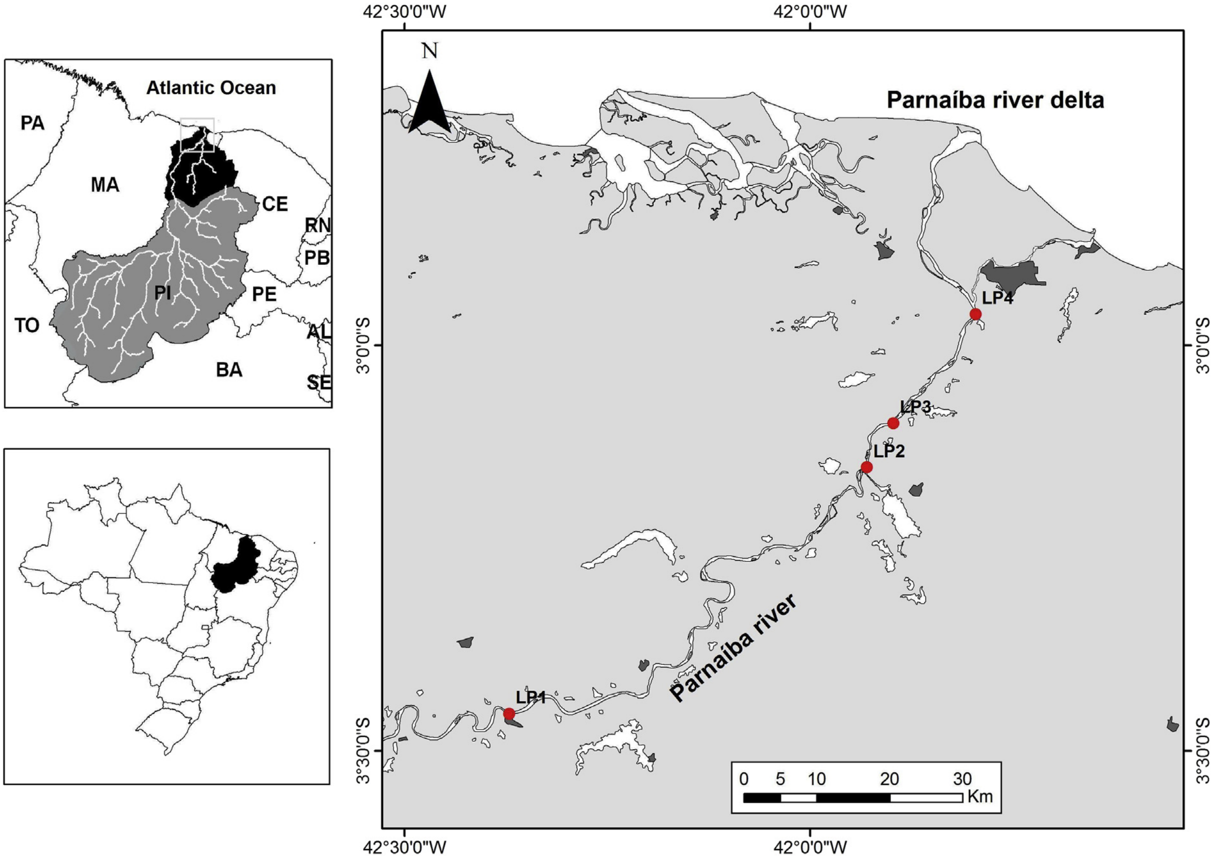


Fig. 1. Brazilian river basins, detailing the lower basin of the Parnaíba River and its estuarine delta and the total N and total P monitoring points in the two sampling surveys conducted between 2010 and 2012.

the annual rainfall in the region (mg m^{-2} $year^{-1}$). It may provide a wide range of values, depending on the degree of urbanization and industrialization of a specific area. In the Brazilian coast they vary from 80 to 300 mg N m^{-2} $year^{-1}$ and from 4 to 10 mg P m^{-2} $year^{-1}$, considering an average rainfall of 1.000 mm $year^{-1}$ (Mello and Almeida, 2004). In our calculations we have used an average emission of 100 N m^{-2} $year^{-1}$ and 8 mg P m^{-2} $year^{-1}$, considering the level of preservation and incipient industrialization and urbanization of the area under study. These values were corrected by the average rainfall in the region. Finally, the deposition fraction reaching the water streams also depends on the soil retention rates, which in this basin correspond to 65% for N and 70% for P (Golley et al., 1978; Malavolta and Dantas, 1980; Silva, 1996).

No dry deposition data is available for the basin of the Parnaiba River. Thus, dry deposition was estimated as proposed by Filoso et al. (2006) for the basin of the Piracicaba River in São Paulo, based on the input of N and P due to wet deposition. We used this assumption in the inventory estimates as dry deposition is likely to be significant in the region, mainly due to the burning of vegetation for land preparation for agriculture, especially in savannah areas where deforestation is most intense (MMA, 2006).

When determining emissions from the physical and chemical denudation of soils (Equation (2)), we considered that agricultural and urban tropical soils under non-mechanized cultivation have an annual soil loss of 128 t km^{-2} $year^{-1}$ (Greenland and Lal, 1977; Goudie, 1987). Losses from urban and agricultural soils can reach rates of 116–309 t km^{-2} yr^{-1} in areas under temperate climate (Schlesinger, 1997) and 60 to 760 t km^{-2} yr^{-1} in tropical regions (Goudie, 1987). An average of about 130 t km^{-2} yr^{-1} was reported for low declivity areas with lack of mechanized agriculture in tropical Africa (Greenland and Lal, 1977). This environmental setting is similar to the Parnaiba basin and coastal plains of northeastern Brazil. Thus, average soil loss rate of 128 t km^{-2} yr^{-1}, as proposed by Goudie (1987), will be used for the calculations of N and P emissions from soil loss in the present study, in a manner similar to other studies carried on in diferent basins of northeastern brazil (Lacerda, 2006; Lacerda et al., 2008; Noriega and Araujo, 2009; Paula et al., 2010).

The concentrations of N and P in the soils vary from 500 to 900 mg g^{-1} for N and from 100 to 500 mg g^{-1} for P, depending on the type of soil (Jacomine et al., 1986; Silva, 1996). The average concentrations of N and P in soils (mg g^{-1}), are respectively: alluvial soils: 900 and 500; Plinthosols/Gleysols: 900 and 100 (Novais et al., 2007); quartz sand dystrophic soils: 500 and 100; Latosols/Podzols: 500 and 500; Solonchack/Solonetz: 500 and 500; Planosols: 500 and 500 (Cantarella, 2007).

$$\mathbb{L}_S^{N,P} = \sum_{j=1}^{9} \rho_{Sj} \cdot A_j \cdot L_S \cdot (1 - \alpha_{rS}) \tag{2}$$

Where $\mathbb{L}_S^{N,P}$ is the total load of N and P supplied by the basin soils to river flows as a function of ρ_{Sj}, which is the concentration of the nutrient in a given soil (mg g^{-1}), A_j is the area corresponding to each type of soil in the basin (km^2), L_S is the average soil loss recorded for gentle tropical slopes and non-mechanized agriculture, similar to the soils in the coastal areas of Northeastern Brazil (Lacerda et al., 2008), and α_{rS} is the soil retention factor (Golley et al., 1978; Malavolta and Dantas, 1980; Silva, 1996). The estimated N load was corrected for NH_3 emissions estimated for nonurban and agricultural areas, considering that a part of natural N emissions can be transferred directly to the atmosphere (Battye et al., 2003; Aneja et al., 2008). An average emission of 5 kg NH_3 ha^{-1} year^{-1} was considered to be lost from areas with non-impacted soils (Schlesinger and Hartley, 1992) according to Equation (3).

$$\mathbb{L}_S^{\boldsymbol{NH}_3} = \boldsymbol{\rho}_{NS}^{\boldsymbol{NH}_3}\cdot\boldsymbol{A}_{NS}\Big/10^3 \tag{3}$$

Where $\mathbb{L}_S^{\boldsymbol{NH}_3}$ is the emission factor of NH_3 for non-cultivated tropical savannah soils, obtained as a function of $\rho_{NS}^{NH_3}$ (Schlesinger and Hartley, 1992) and A_{NS} is the natural forest or non-agricultural soil area in the basin (20.472 ha).

2.2.2. *Anthropogenic sources: wastewater, urban runoff and municipal solid waste (MSW)*

Nutrient emissions by domestic effluents are directly proportional to the concentrations of N or P in wastewater, to the population and to the amount of water consumed per capita (IBGE, 2012), corrected by the 80% rate of return for the water distributed in the water utility network (see Equation (4)). Nutrient concentrations in wastewater were those suggested by Mota and Von Sperling (2009) based on local conditions, whit values of 52 mg l^{-1} and 15 mg l^{-1} for N and P, and a per capita consumption of water o 85 l inhab^{-1} day^{-1} (rural) and 114.2 l inhab^{-1} day^{-1} (urban), according to official data (SNSA, 2012). Finally, the assumption of no-treatment prior to release was used, since the availability of sewage treatment in the northeastern region of Brazil reaches less than 10% of its population (SNSA, 2012).

$$\mathbb{L}_{W_{\mathscr{w}}}^{\boldsymbol{N},\boldsymbol{P}} = \sum_{\boldsymbol{i}=1}^{60}\left(\frac{\boldsymbol{\rho}_{W_{\mathscr{w}}}\cdot\boldsymbol{P}_{\mathscr{u}\boldsymbol{i}}\cdot\boldsymbol{Q}_{\mathscr{u}\boldsymbol{i}}\cdot\beta\cdot365}{10^9}\right)+\sum_{\boldsymbol{i}=1}^{60}\left(\frac{\boldsymbol{\rho}_{W_{\mathscr{w}}}\cdot\boldsymbol{P}_{\mathscr{r}\boldsymbol{i}}\cdot\boldsymbol{Q}_{\mathscr{r}\boldsymbol{i}}\cdot\beta\cdot365}{10^9}\right) \tag{4}$$

Where $\mathbb{L}_{W_{\mathscr{w}}}^{\boldsymbol{N},\boldsymbol{P}}$ is the load of nutrients from wastewater of urban and rural areas of each county within the basin, $\boldsymbol{\rho}_{W_{\mathscr{w}}}$ is the concentration of N or P in raw sewage (mg l^{-1}); $\boldsymbol{P}_{\mathscr{u}\boldsymbol{i}}$ and $\boldsymbol{P}_{\mathscr{r}\boldsymbol{i}}$ are the urban and rural populations, respectively, of each county within the basin; $\boldsymbol{Q}_{\mathscr{u}\boldsymbol{i}}$ and $\boldsymbol{Q}_{\mathscr{r}\boldsymbol{i}}$ are the urban and rural water consumption per capita, respectively; and β is the water/sewage rate of return. Due to the incipient industrialization of the area, effluents from industrial sources were not considered in our calculations as they are a non-significant source of nutrients in this part of the Brazilian coastline.

In order to calculate the nutrient loads in urban runoff, we used the individual urbanization rates of each county within the basin (IBGE, 2012), average annual rainfall (ANA, 2012) and the average concentrations of N and P in urban runoff (NRC, 2000), as shown in Equation (5).

$$\mathbb{L}_{\mathrm{Urf}}^{\boldsymbol{N},\boldsymbol{P}} = \sum_{\boldsymbol{i}=1}^{60}\left(\frac{\boldsymbol{\rho}_{\mathrm{Urf}}\cdot\boldsymbol{A}_{U_{\mathscr{i}}}}{10^6}\right) \tag{5}$$

where $\mathbb{L}_{\mathrm{Urf}}^{\boldsymbol{N},\boldsymbol{P}}$ is the estimated total load of N or P resulting from the runoff of urban areas in each county within the basin; $\boldsymbol{\rho}_{\mathrm{Urf}}$ is the emission factor for N or P obtained from the concentration of each nutrient in urban runoff, i.e. 2.0 mg N l^{-1} and 0.33 mg P l^{-1} (NRC, 2000), and annual rainfall in each county (mm year^{-1}); and $\boldsymbol{A}_{U_{\mathscr{i}}}$ is the urban area of each county within the basin (km^2). The area under study lacks large urbanized areas and the cities in this basin have a low level of soil impermeabilization.

Emissions from solid waste are given as a function of population data (IBGE, 2012), per capita production of waste in each county within the basin, ranging from 0.918 to 1.071 kg inhab^{-1} day^{-1} (ABRELPE, 2011), and a nutrient concentration of 8.9 g N kg^{-1} and 5.6 g P kg^{-1} for fresh waste (Hjelmar et al., 2000). The estimates were corrected by the introduction of factors related to the gravimetric composition of wastes to the rate of soil retention given in Golley et al. (1978); Malavolta and Dantas (1980); Silva (1996) and Hadas et al. (2004). In Brazil, for example, 64% of the MSW is organic (ABRELPE, 2011). Also, a 42% MSW disposal factor, related to the improper waste disposal (ABRELPE, 2011), was introduced as described in Equation (6).

$$\mathbb{L}_{\mathscr{M}SW}^{\boldsymbol{N},\boldsymbol{P}} = \sum_{\boldsymbol{i}=1}^{60}\boldsymbol{\rho}_{\mathscr{M}SW}\cdot\boldsymbol{P_i}\cdot\boldsymbol{G}_{\mathscr{M}SW\boldsymbol{i}}\cdot\boldsymbol{\delta}_{\mathscr{M}SW}\cdot365\cdot(1-\boldsymbol{\alpha}_{\boldsymbol{r}S})\Big/10^9 \tag{6}$$

Where $\mathbb{L}_{\mathscr{M}SW}^{\boldsymbol{N},\boldsymbol{P}}$ is the estimated total N or P load produced by solid waste within the basin as a function of $\boldsymbol{\rho}_{\boldsymbol{m}SW}$, which is the mean concentration of N or P in municipal solid waste (MSW); $\boldsymbol{P_i}$ is the population of each county within the basin; $\boldsymbol{G}_{\mathscr{M}SW\boldsymbol{i}}$ is the per capita production of solid waste in each county corrected by the gravimetric factor, $\boldsymbol{\alpha}_{\boldsymbol{r}S}$ is the soil retention rate, and $\boldsymbol{\delta}_{\mathscr{M}SW}$ is the adequacy factor according to the type of MSW disposal.

2.2.3. *Anthropogenic sources: agriculture*

The use of fertilizers on crops is the main responsible for the flows of N and P to water bodies from agriculture (Filoso et al., 2006; Mizerkowski et al., 2012). Equation (7) was used to calculate the emission estimates from this source.

$$\mathbb{L}_A^{\boldsymbol{N},\boldsymbol{P}} = \sum_{\boldsymbol{i}=1}^{60}\sum_{\boldsymbol{j}=1}^{20}\left(\frac{\boldsymbol{\rho}_{\boldsymbol{tj}}\cdot\boldsymbol{A}_{\boldsymbol{tij}}}{10^3}\right) \tag{7}$$

Where $\mathbb{L}_A^{\boldsymbol{N},\boldsymbol{P}}$ is the total N or P loads from the 20 most common crops ($\mathscr{j}$) cultivated in the 60 counties ($\boldsymbol{i}$) of the region (i.e. rice, beans, cassava, sugarcane, corn, banana, cashew, soybean, fruits, etc.), $\boldsymbol{\rho}_{\boldsymbol{tj}}$ is the emission factor of N or P applied as fertilizer (kg ha^{-1}) and the loss percentage according to crop type, and $\boldsymbol{A}_{\boldsymbol{tij}}$ is the cultivated area (ha.year^{-1}) of each crop type in each county within the basin (IBGE, 2012). Nitrogen emissions were adjusted for the volatilized NH_3 losses, as close to 30% of the applied nitrogen fertilizer is lost by volatilization as NH_3 and NO_x (Mikkelsen, 2009), part is incorporated by the crops, part is retained by the soil and the remaining is lost to the water streams.

2.2.4. *Anthropogenic sources: livestock farming*

Livestock farming emissions of N and P described in Equation (8) depend on the concentrations of each nutrient in animal manure, which are relatively constant (EMBRAPA, 2004), on the soil retention rate (Malavolta and Dantas, 1980; Silva, 1996), and in the case of N on the losses to the atmosphere in the form of reactive nitrogen, particularly ammonia (Faulkner and Shaw, 2008).

$$\mathbb{L}_{\mathscr{H}}^{\boldsymbol{N},\boldsymbol{P}} = \sum_{\boldsymbol{i}=1}^{60}\sum_{\boldsymbol{j}=1}^{60}\boldsymbol{\rho}_{\mathscr{t}\boldsymbol{j}}\cdot\mathscr{H}_{\boldsymbol{ij}}\cdot(1-\boldsymbol{\alpha}_{\boldsymbol{r}S})\Big/10^9 \tag{8}$$

Where, $\mathbb{L}_{\mathscr{H}}^{\boldsymbol{N},\boldsymbol{P}}$ is the estimated total load of N or P from animal manure in the region (i.e. poultry, meat cattle, dairy cattle, goats, sheep and swine), $\boldsymbol{\rho}_{\mathscr{t}\boldsymbol{j}}$ is the emission factor related to the annual quantity of manure produced per animal in each county within the basin ($\boldsymbol{j}$) and the concentration of N or P in raw manure (mg kg^{-1}); $\mathscr{H}_{\boldsymbol{ij}}$ is the number of animals in each county within the basin ($\boldsymbol{i}$); and $\boldsymbol{\alpha}_{\boldsymbol{r}S}$ is the N and P soil retention rate (Malavolta and Dantas, 1980; Silva, 1996). Equation (9) presents the adjustment due to volatilized ammonia from manure of the six main animals grown in the basin.

$$\mathbb{L}_{\mathscr{H}}^{\boldsymbol{NH}_3} = \sum_{\boldsymbol{i}=1}^{60}\sum_{j=1}^{6}\left(\boldsymbol{\rho}_{\mathscr{A}\boldsymbol{j}}^{\boldsymbol{NH}_3}\cdot\mathscr{H}_{\boldsymbol{ij}}\Big/10^3\right) \tag{9}$$

The loss of ammonia due to volatilization, i.e. $\mathbb{L}_{\mathscr{H}}^{\boldsymbol{NH}_3}$, is obtained as a function of $\boldsymbol{\rho}_{\mathscr{A}\boldsymbol{j}}^{\boldsymbol{NH}_3}$, which is the emission factor for each type of animal (kg NH_3 animal^{-1} year^{-1}) and $\mathscr{H}_{\boldsymbol{ij}}$, which is the number of heads of each type of animal in each county within the basin.

2.2.5. *Anthropogenic sources: shrimp farming*

The loads were estimated from local or regional emission factors according to pond area and type of management, classified as extensive, semi-extensive, semi-intensive and intensive (Cunha, 2010), according to Equation (10).

$$\mathbb{L}_{aq}^{\boldsymbol{N},\boldsymbol{P}} = \sum_{\boldsymbol{j}=1}^{4}\boldsymbol{\rho}_{aq\boldsymbol{j}}\cdot\boldsymbol{A}_{sp\boldsymbol{j}} \tag{10}$$

Where $\mathbb{L}_{aq}^{\boldsymbol{N},\boldsymbol{P}}$ is the estimated total load of N or P from shrimp farming (t year^{-1}), $\boldsymbol{\rho}_{aq\boldsymbol{j}}$ is the emission factor that relates the concentration of nutrients in the effluents according to the farmings system ($\boldsymbol{j}$), the pond water renewal rate ranging from 5 to 10% daily and 2.5 production cycles per year, which is the norm in the Brazilian Northeast (Lacerda et al., 2006; Cunha, 2010); and $\boldsymbol{A}_{sp\boldsymbol{j}}$ is the area of the shrimp farming ponds of each farming system in the Parnaíba River Delta (Sampaio et al., 2008).

2.3. *Calibration of results*

The accuracy of the estimates was determined from the relationship between the flows estimated through emission factors and the flows measured in situ ($Q_{\boldsymbol{e}}/Q_{\boldsymbol{m}}$) in two different hydrological periods (dry and rainy seasons), The flows were calculated from the concentrations of total N and P in water samples collected in four sampling points upstream to the Parnaiba River Delta, considering the historical average flow of the last 25 years available in the HidroWeb web portal: http://hidroweb.ana.gov.br/ (ANA, 2012).

Water samples were collected in duplicate using Van Dorn bottles, stored in amber glass bottles and preserved at 4 °C in a thermal box. In the laboratory, samples were analyzed in triplicate for Total P and Total N by wet oxidation with potassium persulfate ($K_2S_2O_8$) in an alkaline medium (Valderrama, 1981). After digestion, the total P concentration was measured by spectrophotometry in the visible range, according to the molybdate blue method (Grasshoff et al., 1999), while the total N concentration was determined by the sodium salicylate method (Müller and Wiedemann, 1955).

3. Results

3.1. *Natural emissions: atmospheric deposition and soil denudation*

The estimated atmospheric inputs corresponded to 1.726 t N year^{-1} and 118 t P year^{-1}. This means that atmospheric deposition is the N natural source with greater relevance, reaching 69% of all natural nitrogen inputs to the basin. The emissions of nutrients in the basin by area corresponded to 40.3 kg N km^{-2} year^{-1} and 2.8 kg P km^{-2} year^{-1}. The total atmospheric deposition of N (NH_x and NO_y) to the lower basin of the Parnaíba River was below the 100–175 kg N km^{-2} year^{-1} range reported by Filoso et al. (2006) for the coastline of NE Brazil and is about 8 times lower than the average deposition rate of 325 kg N km^{-2} year^{-1} reported for Brazil. Overall, our results were below those reported by Caraco and Cole (1999) for 35 major river systems worldwide, with values ranging between 50 and 2.700 kg N km^{-2} year^{-1} and average 743 kg N km^{-2} year^{-1}. When it comes to P, the estimated value was about 4 times lower than that reported by Mizerkowski et al. (2012) for the Paranaguá river basin (11 kg P km^{-2} year^{-1}) in southern Brazil.

When comparing the loads normalized by area with those of other Brazilian semiarid coastal basins, it shows that atmospheric inputs in the low Parnaiba exceeded those found in the basins of the Açu River/RN (State of Rio Grande do Norte – basin area: 950 km^2), i.e. 25 kg N km^{-2} year^{-1} and 1.7 kg P km^{-2} year^{-1}, and Jaguaribe River/CE (State of Ceará – basin area: 1.735 km^2), i.e. 12 kg N km^{-2} year^{-1} and 0.9 kg P km^{-2} year^{-1}. These two basins have a similar development level than the Parnaiba's (Lacerda et al., 2006, 2008). Likewise, they are beyond those reported by Noriega and Araujo (2009) for the Capiberibe River basin (state of Pernambuco – basin area: 7.557 km^2), i.e. 26 kg N km^{-2} year^{-1} and 1.9 kg P km^{-2} year^{-1} and by Cunha (2010) for the Potengi River basin/RN (basin area: 934 km^2), i.e. 37 kg N km^{-2} year^{-1} and 2.4 kg P km^{-2} year^{-1}. These two basins include regional metropolitan areas, resulting in a higher N atmospheric deposition.

The physical and chemical denudation of soils provides an important contribution to the natural transfer of N and P to coastal areas through river flows. This process is influenced by soil type, vegetation and climate, and is accelerated by increased urbanization and deforestation, with varying values for temperate and tropical regions (Silva, 1996). The total emissions from soil denudation are presented by soil type in Fig. 2, being 772 t N year^{-1} (corrected for the loss of NH_3) and 660 t P year^{-1}. A correction of 296 t year^{-1} was considered for nitrogen soil emissions related to the outflow of N–NH_3 from the basin's non-agricultural and forested lands. Even though we considered a nitrogen correction, we should note that there is a high dose of uncertainty involving the estimates of NH_3 emissions from non-agricultural or forested areas, because of the ability of soils and plants to act as both sources and sinks of NH_3. Moreover, the use of a single emission factor does not take into account the characteristics of the different soil types in the basin, thus providing only an approximation of such emissions. On the other hand, as the acidic soils of the region have a high retention capacity, P emissions are transferred to the water streams mostly associated to suspended particles in the form of particulate phosphorus, giving this nutrient a practically conservative behavior (Paula Filho et al., 2012).

According to these considerations, our estimates show that the greatest losses of N are associated with neosols (Ne) and plinthosols (Pt), with emissions of 190 t year^{-1} (25%) and 172 t year^{-1} (23%),

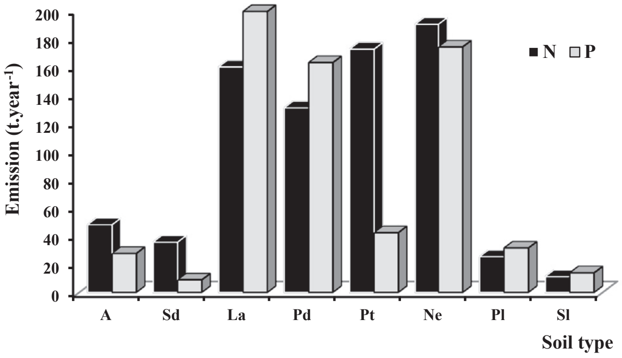


Fig. 2. Emissions of N and P from the different soil types typical of the lower basin of the Parnaíba River (A – alluvial; Sd – sands; La – latosol; Pd – podsol; Pt – plintosol; Ne – neosols; Pl – planosol; Sl – solonetz).

followed by latosols (La) with 160 t year^{-1} (21%) and podzols (Pd) with 131 t year^{-1} (17%), these account for 88% of total P released, with loads equal to 199 t year^{-1} (La), 174 t year^{-1} (Ne), 163 t year^{-1} (Pd) and 42 t year^{-1} (Pt).

These results indicate that the basin's soils are the main natural source of P to surface waters, representing 85% of all natural inputs. Emissions by basin area correspond to 18 kg N km^{-2} year^{-1} and 15.4 kg P km^{-2} year^{-1}. N and P emissions reported for the non-mechanized agriculture basins of the Atlantic eastern coast of the Brazilian NE region vary from 30 to 100 kg N km^{-2} year^{-1} and 1–60 kg P km^{-2} year^{-1} (Lacerda et al., 2008; Noriega and Araujo, 2009). The nitrogen emissions estimated in this study were below such range, while P was within the range of emissions reported for the coastal basins of NE Brazil. These results reflect the characteristics of the coastal soils, which are highly weathered (latosols and podzols), generally dystrophic, with a low nutrient availability and susceptible to erosion with a consequent loss of nutrients associated to mineral particles (Jacomine et al., 1986). Comparing this basin with other basins of regional importance, the normalized values were lower than those reported for the Açu River basin/RN, with 98 kg N km^{-2} year^{-1} and 59 kg P km^{-2} year^{-1}, the Jaguaribe River basin/CE, with 71 kg N km^{-2} year^{-1} and 26 kg P km^{-2} year^{-1}, the Potengi River basin/RN, with 34 kg N km^{-2} year^{-1} and 30 kg P km^{-2} year^{-1} and the Ceará River basin/CE, with 80 kg N km^{-2} year^{-1} and 70 kg P km^{-2} year^{-1} (Lacerda et al., 2006, 2008), reflecting the more intensive use of the soil in these basins compared to the Parnaíba River.

3.2. Anthropogenic emissions: domestic wastewater, urban runoff and municipal solid waste (MSW)

Since less than 10% of the population in this basin and in the Brazilian northeast region counts with domestic sewage treatment and is mainly restricted to metropolitan areas not included in this study (SNSA, 2012), we considered that no sewage treatment whatsoever was applied before the release of the effluents into the water courses of the region. Another issue is that human sewage does not represent new or imported inputs of N and P to the basin (Howarth et al., 1996). Urban emissions totaled 1.215 t N year^{-1} and 340 t P year^{-1}, while rural emissions added up to 736 t N year^{-1} and 206 t P year^{-1}. This represents 17.1% and 6.8% of N and P, respectively, of all anthropogenic emissions (Fig. 3). Our estimates project a sewage discharge per capita of 4 g N inhab^{-1} day^{-1} and 1.1 g P inhab^{-1} day^{-1}, comparable to those reported by Howarth et al. (1996) (9.1 g N inhab^{-1} day^{-1}) and Smil (2000) (1.5 g P inhab^{-1} day^{-1}) in their global emission estimates for these nutrients.

The indicated loads are lower than those reported for coastal basins that include urban centers and metropolitan areas, such as the Capibaribe/PE and Cocó/CE river basins. In the Capibaribe River basin, which includes Recife's metropolitan area, the emissions from sewage account for 4.965 t N year^{-1} (72% of all anthropic contributions) and 993 t P year^{-1} (68%) (Noriega and Araujo, 2009), while in the Cocó River, located in the metropolitan area of Fortaleza, such emissions account for 2.116 t N year^{-1} (82%) and 596 t P year^{-1} (80%) (Lacerda et al., 2008).

Waters from urban runoff are a nonpoint source of pollutants that can significantly influence the quality of the receiving water bodies. This source has grown with the expansion of urban areas while several factors determine the magnitude of the N and P inputs, such as the level of soil permeability and the nature of the drainage system (Oishi, 1996). Nutrient loads from urban runoff and municipal solid waste (MSW) were 167 t N year^{-1} and 25 t P year^{-1}, and 384 t N year^{-1} and 208 t P year^{-1}, respectively. Together, these sources account for 5% and 3% of the N and P emitted by the basin.

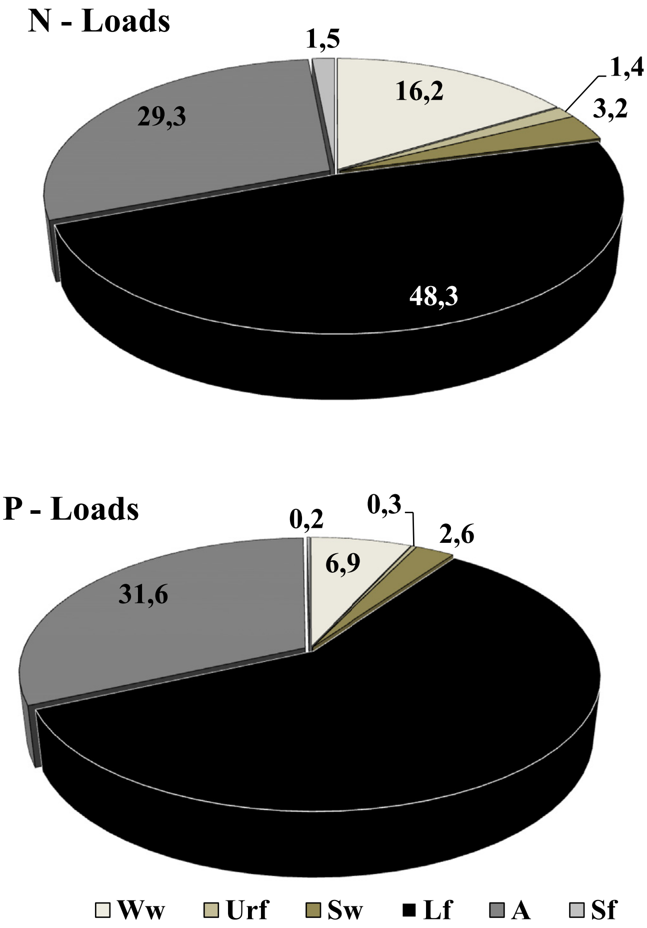


Fig. 3. Relative N and P contributions of the different anthropogenic sources: domestic wastewater (Ww), disposal of municipal solid waste (Sw), runoff from urban areas (Urf), agriculture (A), livestock farming (Lf) and aquaculture (Sf).

The runoff discharges 3.9 kg N km^{2} year^{-1} and 0.6 kg P km^{2} year^{-1}, while municipal solid waste emits 9 kg N km^{2} year^{-1} and 4.9 kg P km^{2} year^{-1}, figures similar to the values reported for the basins of the West Atlantic coastline of NE Brazil, which is not too urbanized (Lacerda et al., 2006).

3.3. Anthropogenic emissions: agriculture

In non-industrialized, scarcely urbanized areas, emissions from agriculture and livestock farming activities represent an important source of N and P to the rivers. Their emissions vary according to soil type, crop management system, planting area of each particular crop, and herd size and type. The emission factors available for agriculture are variable and depend on the agricultural practice employed (i.e. conventional or direct, mechanized or traditional tillage). Moreover, the type of crop indicates the nutrient loss rates (Malavolta and Dantas, 1980) as each particular crop requires a particular amount of fertilizer (EMBRAPA et al., 2003). In the studied basin, some reports have summarized the usual quantities of fertilizer used in most present crops (Table 1). The estimated amount of nutrients lost to estuary in of basin is a function of these differences in culture type and their relative area of cultivation.

Even though the area occupied by crops is less than 8% (331.730 ha) of the basin, the emission of nutrients due to the application of chemical fertilizers is significant, ranking second in

Table 1
Agronomic recommendations (kg ha^{-1}) and loss rates (%), by the use of nitrogen and phosphate fertilizers, in major agricultural crops grown in the Parnaíba Basin, NE Brazil.

Crop	Fertilizer recommendations (kg ha^{-1})		Loss (%)	
	N	P	N	P
Cotton[a]	22	12	16	6.0
Rice[a]	90	150	20	10
Sweet potato[a]	20	90	20	10
Banana[a,b]	100	30	20	10
Coconut[a,b]	40	20	25	20
Sugar cane[a,c]	182.5	30	29	13
Cashew nut[a,b]	20	30	20	25
Bean[a]	10	60	21	1.0
Cassava[a]	20	37.5	25	20
Guava[b]	100	30	20	10
Orange[a,b]	150	45	21	1.1
Lemon[a,b]	150	45	21	1.1
Papaya[b]	100	30	20	10
Mango[a,b]	40	20	16	6.0
Watermelon[a,b]	100	30	20	10
Melon[a,b]	65	70	20	10
Corn[a]	100	30	20	10
Sorghum[a]	100	30	20	10
Tomato[a]	100	30	20	10
Tangerina[b]	150	45	21	1.1
Soybean[a]	20	100	16	10

[a] Agronomic recommendations for application of fertilizers in different crops grown in the region and their loss rates, with data available in Embrapa Production Systems, (https://www.spo.cnptia.embrapa.br/).
[b] EMBRAPA, 2009.
[c] Malavolta and Dantas, 1980.

importance in N and P emissions to surface and coastal waters. Sustainable development statistical data in Brazil report rates of application of chemical fertilizers of 74.5 kg ha^{-1} for the Parnaiba River basin, representing 21 kg N ha^{-1} and 25 kg P ha^{-1} (IBGE, 2012). According to the planted area (ha), the application of fertilizers added up to 7.000 t N $year^{-1}$ and 8.300 t P $year^{-1}$.

The estimates obtained from the nitrogen applied on the main crops cultivated in the region (Equation (7)) (i.e. rice, corn, soybean, sugarcane, beans, fruits and vegetables, as shown in Table 1), accounted for 3.524 t N $year^{-1}$ (50%), already corrected for the loss of N–NH_3, 1.510 t N $year^{-1}$ or 22% of the total applied. The proportion of nitrogen lost from N fertilizers due to NH_3 volatilization may can reach more than 50%, depending on fertilizer type, environmental conditions (i.e. temperature, wind speed, rain), and soil properties (calcium content, cation exchange capacity, acidity) (Viero et al., 2014). The efficiency of the recovery of nitrogen to the soil by plants is generally less than 50% (Bredemeier and Mundstock, 2000). The uptake of the N applied through mineral fertilizers by plants ranges from 20% to 40% (Vlek and Byrnes, 1986), thus among 1.400–2.800 t N $year^{-1}$ was incorporated by the crops in the 2010 harvest. P losses in the same period were 2.517 t P $year^{-1}$ or 30% of the total applied, while the rest was taken up by the plants (10–25%) or fixed by the soil (Brady and Weil, 1996). The variety of fertilizer recommendations and the diversity of factors that may influence fertilizer leaching losses in agricultural systems represent a significant source of uncertainty in any estimate made using emission factors. For example, Howarth et al. (1996) reported losses of 10%–40% in argisols and 25%–80% in sandy soils in temperate regions of the North Atlantic. In tropical soils in Southeast Brazil, fertilizer losses range from 6% to 20% for P and 26%–32% for N (Malavolta and Dantas, 1980; EMBRAPA, 2003). The crop type influences the loss rates of nutrients, since different cultures require different amounts of fertilizer application.

3.4. *Anthropogenic emissions: livestock farming*

Livestock farming is a significant economic activity throughout the Parnaíba basin, mainly bovine, goat and swine herds. Nitrogen and phosphorus emissions for each livestock farming is shown in Table 2. This activity is the most important anthropogenic source of nutrients to the soil and eventually to surface waters, providing around 43% and 58% of the total N and P emitted by anthropogenic sources (Fig. 3), which may affect the hydrochemistry of estuaries. Part of these nitrogen emissions are deposited in the soil, incorporated by plants or lost to the atmosphere (IPCC, 2006). The total flow of N and P from livestock farming, based on Equation (9) and corrected by N–NH_3 losses estimated at 1.730 tons (Equation (10)), corresponded to a net load of 4.668 t N $year^{-1}$, while P emissions added up to 4.658 t P $year^{-1}$. The cattle industry is the most significant activity, accounting for 44% and 47% of N and P emissions, respectively, followed by poultry with 21% of the industry's emissions.

The values for N shown in Table 2 were corrected for the loss of N–NH_3 to the atmosphere, which is an important outflow in tropical environments. The hot and humid climate of the Brazilian NE region, with an average annual temperature of around 27 °C, favors higher emissions by volatilization. In our study, the average loss was 61% of the nitrogen entered to the basin from animal manure, which is within the range reported for N volatilization losses (NH_3 and NO_x) by the Guidelines for National Greenhouse Gas Inventories (IPCC, 2006). However, similar studies in other basins of the Brazilian NE did not take into account the outflow of N through volatilization and may have overestimated the emissions of N for this activity (Lacerda et al., 2006, 2008; Noriega and Araujo, 2009; Paula et al., 2010).

3.5. *Anthropogenic emissions: shrimp farming*

Shrimp farms are significant sources of nutrients with potential adverse effects on coastal environments (Thomas et al., 2010). This industry uses large amounts of fertilizers to maintain high productivity levels. Moreover, the volume and quality of wastewater generated by shrimp farms depend on the type of management and intensity, i.e. the more intensive, the higher the discharge of effluents in the receiving water body (Cunha, 2010). Estimates of loads related to shrimp farming in the Parnaiba River Delta are presented in Table 3, where they are compared to other areas of the NE coast of Brazil. This industry has a pond area of 754 ha, distributed among the states of Maranhão and Piauí (Sampaio et al., 2008).

Table 2
N and P emissions (t $year^{-1}$) from livestock farming in the low Parnaíba River basin in 2010.

Animal	Heads (×10^3)[a]	N[b]	P[b]
Poultry	3778	934	968
Meat cattle	498	2059	2183
Dairy cattle	42	253	183
Goats	501	161	274
Equine	74	417	324
Swine	629	732	516
Sheep	256	112	210

[a] Rural census (IBGE, 2012).
[b] Daily production of manure (kg $animal^{-1}$ day^{-1}): bovine/equine = 10; swine = 2.5; goats and sheep = 1.0; poultry = 0.18 (EMBRAPA, 2004; FAO, 2012); Concentration of N and P in manure: bovine/equine = 0.6 and 0.4%; swine = 0.5 and 0.3%; goats and sheep = 0.5 and 0.5%; poultry = 1.2 and 1.3% (EMBRAPA, 2004; Galvão et al., 2008); soil retention factor: N = 0.65 and P = 0.7; N–NH_3 emission (kg NH_3 $head^{-1}$ $year^{-1}$): bovine = 4.3, dairy cattle = 5.6; equine = 7.0, poultry = 0.1, goats = 1.1, sheep = 0.7, swine = 1.5 (Faulkner and Shaw, 2008; Aneja et al., 2008).

The results presented in Table 3 show that despite the high annual loads of N and P emitted by this industry, the relative contribution of shrimp farming to the delta is significantly lower than those recorded in the Jaguaribe/CE, Açú/RN and Curimataú/RN river basins, mainly due to the type of farming. The most commonly used farming system in the low Parnaiba is semi-intensive, while in the other basins shrimp farming is intensive, resulting in different emission factors due to the different concentrations of nutrients of each type of pond management. Aquaculture, and especially shrimp farming, has a significant economic importance in some states of the Brazilian Northeast. Therefore, the determination of the N and P loads emitted by the industry is critical in determining the carrying capacity of estuaries where the farms are located.

3.6. *Calibration of the inventory results*

In the four sampling points monitored in both campaigns ($n = 8$), the average concentrations ranged from 0.19 to 0.29 mg N L^{-1} (median, 0.26 mg N L^{-1}) and 0.16–0.20 mg P L^{-1} (median, 0.17 mg P L^{-1}) including the results of September 2010 (dry season) and March 2012 (rainy season). The historical average flow for the last 25 years obtained from the HIDROWEB web portal (http://hidroweb.ana.gov.br/) was 770 m^3 s^{-1}. The N and P flows for the Parnaiba River Delta, obtained from the concentration data, corresponded to 6.387 t N $year^{-1}$ and 4.160 t P $year^{-1}$.

4. Discussion

4.1. *Total N and P emissions to the Parnaiba River Delta*

The total loads of N and P from natural sources to the Parnaíba River Delta reflect the contributions of chemical elements through physical and chemical soil denudation mechanisms and atmospheric sources, which total contribution amounted to 2.499 t N $year^{-1}$ and 778 t P $year^{-1}$. The loads related to natural processes are directly affected by the region's soil characteristics and climate dynamics. The atmospheric deposition of N was 69% higher than the natural intake of this nutrient from the soil. We must highlight that even though part of the N naturally enters the atmosphere through ammonia volatilization, microbial generation of nitrogen dioxide in the soil and the release of N-containing particles by wind action, there are N sources to the atmosphere that are anthropogenic in nature. Estimates made for the Northern Hemisphere indicate that up to 80% of N atmospheric emissions are anthropogenic (Jickells, 2006). The contribution of P from physical and chemical soil denudation was almost 5.6 times higher than atmospheric emissions. As P does not suffer volatilization losses and its leaching losses are usually very low, the erosion of soils and runoff are by far the most important sources for P flows into the oceans (Smil, 2000).

Table 3
Comparison of N and P load estimates (t $year^{-1}$) and relative importance (%) of emissions from shrimp farms installed in the coastal areas of northern of Brazil.

Basin	Pond area (ha)	Total load – t $year^{-1}$ (%)	
		N	P
Low Parnaiba/PI/MA[a]	754[e]	181 (2)	15 (0.2)
Jaguaribe/CE[b]	1640	346 (41)	29 (8)
Acaraú/CE[b]	743	188 (12)	16 (2)
Açú/RN[c]	1679	411 (63)	35 (13)
Curimataú/RN[c]	1070	248 (20)	23 (7)
Potengi/RN[d]	753	202 (6)	15 (2)

[a] This study.
[b] Lacerda et al. (2008).
[c] Lacerda et al. (2006).
[d] Cunha (2010).
[e] Sampaio et al. (2008).

Regionally, natural loads are significant when compared to the contributions of coastal basins of the western coastline of the Brazilian NE region, involving the states of Ceará, Rio Grande do Norte, Paraíba and Pernambuco (Fig. 1). According to Lacerda et al. (2008), the coastal basins of Ceará contribute with about 1.503 t N $year^{-1}$ and 971 t P $year^{-1}$ (15 basins). Lacerda et al. (2006) and Cunha (2010) attribute flows of 394 t N $year^{-1}$ and 155 t P $year^{-1}$ to the 7 major basins of the state of Rio Grande do Norte, while Noriega and Araujo (2009) estimated flows of 2.160 t N $year^{-1}$ and 79 t P $year^{-1}$ (12 basins) for the coastal basins of the state of Pernambuco. Estimates of N and P exports in the regional basins were obtained from the data available for each region instead of using a uniform approach. Therefore, the quality of the estimates varies among the different regions. Details and most data sources are described by Lacerda et al. (2006).

Fig. 3 shows the relative contributions of N and P emissions of the major anthropogenic sources to the Parnaíba River Delta. In our inventory we considered emissions associated with domestic wastewater (Ww), disposal of municipal solid waste (Sw), runoff from urban areas (Urf), agriculture (A), livestock farming (Lf) and aquaculture (Sf). The relative contribution of each source varies according to the extent of agricultural areas, the level of urbanization, sanitation and population density.

The total flow of nutrients to the lower basin of the Parnaíba River Delta from anthropogenic sources added up to 12.019 t N $year^{-1}$ and 7.970 t P $year^{-1}$. These flows are in the same order of magnitude than those reported for other basins of the western coast of the Brazilian NE region. Anthropogenic loads estimated for the basins in the state of Ceará were 12.622 t N $year^{-1}$ and 6.704 t P $year^{-1}$ (Lacerda et al., 2008), while for the state of Rio Grande do Norte they totaled 8.920 t N $year^{-1}$ and 5.443 t P $year^{-1}$ (Lacerda et al., 2006; Cunha, 2010). However, our N anthropogenic emissions estimates differ by one order of magnitude from those reported for the basins in the state of Pernambuco (34.025 t N $year^{-1}$ and 6.713 t P $year^{-1}$) (Noriega and Araujo, 2009). These results suggest the existence of a latitudinal gradient of nitrogen flows, i.e. from the Parnaíba basin to the western coast basins of the NE region, associated with a more intensive urban and industrial use of the land and smaller river flows.

The relative contributions of each anthropogenic source to the N and P emission estimates presented in Fig. 3 show livestock farming as the main source of N and P to surface waters in the lower Parnaíba River, followed by agriculture. These results support the scenario proposed by the Global NEWS model, which demonstrated the importance of these sources for anthropogenic fluxes of N and P in watershed areas with low development, reflecting the rapid growth of livestock production and less efficient use of nutrients in agriculture (Seitzinger et al., 2005, 2010). Domestic sewage ranks as the third largest source of N and P to the system, while shrimp farming is a more significant source of N than P. Urban solid waste and runoff account together for less than 5% and 3% of the N and P emissions, respectively.

4.2. *Accuracy of N and P flow estimates to the Parnaiba River Delta*

The accuracy of the N and P flow estimates for the coastal region of the basin of Parnaiba checked out when compared to the flows of N and P measured upstream to the delta. The results of the measured Total N and Total P are consistent with the estimated values. The total flows estimated in this study (natural + anthropogenic) through emission factors accounted to 14.518 t N $year^{-1}$ and 8.748 t P $year^{-1}$, while the measured concentrations amounted to 6.083 t N $year^{-1}$ and 4.259 t P $year^{-1}$.

The ratios between the estimated and measured values of N and P were 2.4 and 2.1, respectively, representing a reasonably accurate result considering the uncertainties surrounding the methodology, especially those associated with the use and scope of regional and global data. The observed discrepancies can be explained as the action of buffer areas (wetlands) and retention, assimilation and transformation mechanisms of nutrients that are inherent to these areas (Reddy et al., 1999). The retention of nutrients varies greatly according to the watersheds. Rivers with high specific flow and a minor area of lakes within the catchments have in general lower retention of nutrients than rivers with a large number of lakes and low specific flow. Salomons (2004), in the context of EuroCat Project, which estimated emissions of N and P from point and diffuse sources of the rivers Vistula, Rhine-Elbe, Po, Provadijska, Humber, Idrijca and Axios to the European coast, found an average retention of 33% for the N. Highest retention values were observed in basins of rivers Provadijska (86%) and Axios (61%), related to the presence of large lakes and medium sized reservoirs in the catchments, which probably causes the high retention (higher denitrification) of nitrogen. Nutrient retention by artificial dams, common in the semiarid regions of Brazil, also contributes to the outcome, reducing the rates of export to tributary basins. In the case nitrogen, significant losses due to [NO_3^- to N_2] conversion (denitrification) can account for 30%–70% of the removal of the nitrogen transported from the basin to the river and then to the estuary (Galloway et al., 2003). Large floodplain areas are also typical of these semiarid basins due to strong seasonal fluctuation of water levels. These characteristics contribute with higher retention rates of nutrients within the basins before reaching the river. Furthermore, the extensive mangrove areas of the Parnaíba Delta contribute greatly to reducing the effects of loads of N and P in the coastal environment. This wetland ecosystem, in particular the soil component, is considered a nutrient sink, which could alleviate the detrimental impact of sewage discharges to the surrounding environment. The mechanisms involved in the retention of nutrients in wetlands correspond to adsorption on exchange sites and biding to organic matter, biological oxidation and mineralization, nitrification and denitrification and precipitation (Tam and Wong, 1996). In addition, alluvial sediments rich in iron oxy-hydroxides, are the prime substrates for phosphate sorption in estuaries, such as the Parnaíba Delta (de Paula Filho, 2015).

A comparison with other tropical basins in northeastern Brazil (Fig. 4) shows livestock farming and agriculture as the main sources of nutrients to the coastal zone in these regions. The Parnaiba basin had higher loads from livestock compared to other basins in the northeastern states (179 kg N km^{-2} yr^{-1} and 75 kg P km^{-2} yr^{-1}).

Finally, even though the TP and TN measurements were made in different hydrological periods, they correspond to flash flows, which may not include higher loads contributed by the Parnaíba River, which are typically transported in periods of intense rainfall. Therefore, to better estimate their loads it is necessary to increase the sampling period, seeking to build a more realistic picture of nutrient flow from the basin to the Parnaíba River estuary. However, even considering the differences between the estimates and the values measured in situ, the results were quite consistent and capable of generating actual scenarios for control and management decision-making purposes involving point and nonpoint sources in this important portion of the Northeastern coast of Brazil.

4.3. Inclusion of the coastal basins in NE Brazil within the global scenario of continental flows to the Atlantic Ocean

The N and P flows estimated in this paper correspond to 339 kg N km^{-2} year^{-1} and 204 kg P km^{-2} year^{-1}, while the eastern coastal basins of the Brazilian NE show highly variable N and P flows, ranging from 259 to 7.346 kg N km^{-2} year^{-1} and 151 to 1.821 kg P km^{-2} year^{-1}.

The coastal megabasins model (COSCATs) proposed by Meybeck et al. (2006) grouped the Parnaíba river basin and the Eastern and Western Atlantic coast basins of the Brazilian NE region together and classified them as “meso-active” with regard to the transfer of nitrogen, similarly to Coral, North Sea, N. South China Sea, W. Yellow, New England, Rio de la Plata, E. Yellow Sea, NW Okhotsk, W. Deccan, E. Deccan Niger Delta. This rating scale involves eight categories obtained according to the Y_i/Y^* ratio (local flow/average global flow), where a meso-active basin is in the range of $0.5 < Y_i/Y^* < 2$. When we refine the model to the regional level and considering a value of $Y^* = 355$ kg N km^{-2} year^{-1} for exoreic basins (Green et al., 2004), the calculated ratio for the coastal basin of the Parnaíba River is 0.95, thus confirming the proposed classification. On the other hand, the eastern coastal basins of the Brazilian NE region showed a wide range of classifications, i.e. “meso-active”, “eury-active”, “hyper-active” and even “hot spots” for the transfer of materials with a Y_i/Y^* ratio >10, such as basins that include large cities and metropolitan areas. Following the same reasoning for P and with $Y^* = 95$ kg P km^{-2} year^{-1} (Seitzinger et al., 2005), the basin can also be classified as “eury-active” in terms of P flows, $Y_i/Y^* = 2.15$ kg P km^{-2} year^{-1}.

5. Conclusions

In a scenario of regional and global changes, the evidence gathered in this study suggests that the biogeochemical cycles of N

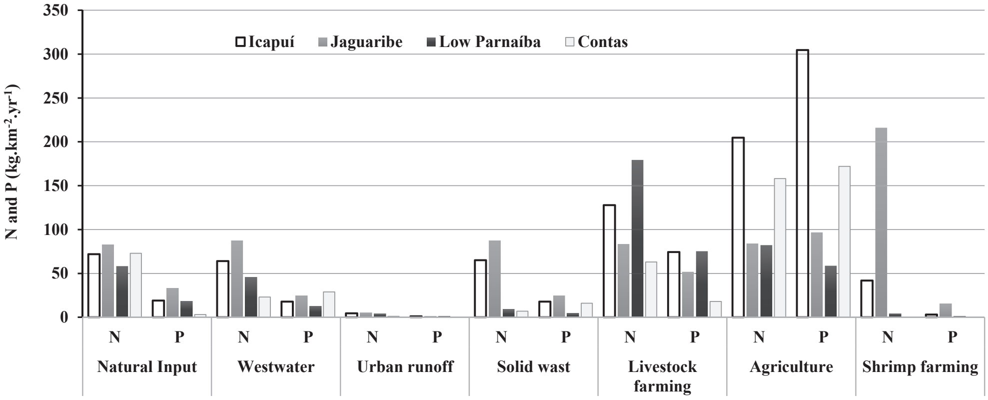


Fig. 4. Comparison of N and P emissions (kg km^{-2} yr^{-1}) from basins in four sites in northeastern Brazil. Icapui and Jaguaribe basin (Lacerda et al., 2008); Conta basin (Paula et al., 2010); Low Parnaiba (this study).

and P in tropical developing countries are increasingly less controlled by natural processes and more by human activities mobilizing these contaminants in the environment. Although the basin is not a very populated area, having a population density of 31 inhab km^2 and an incipient industrial development, the anthropogenic emissions of N and P are important sources of nutrients to its estuarine region, mainly due to the increased use of agriculture consumables, livestock farming and untreated wastewater discharges to its water courses, altering the water quality of the estuaries.

N and P contributions of predominantly rural human activities (agriculture, livestock and shrimp farming) are approximately 3.8 and 9.3 times higher than urban inputs (wastewater, runoff and municipal solid waste), respectively, together accounting for 66% of the N and 82% of the P released to the estuary. Regarding total nutrient emissions, anthropogenic sources account for 83% of N and 91% of P, 4.8 and 10.2 times higher than the natural contributions of N and P to the basin, respectively. Similarly to other basins in the western coast of the Brazilian NE region, except for major metropolitan areas where wastewater contributions prevail, the results showed a strong influence of agriculture and livestock farming on nutrient emission.

The use of load estimates obtained from emission factors represents a satisfactory approach to assess the inputs of N and P (both natural and anthropogenic) and provide an important foundation for the development of national and regional strategiesfor the management of water resources and the environment, especially in areas where monitoring programs and official information on the concentrations of these nutrients are scarce, as in the Parnaíba River Delta Region. This is essential for the formulation of scenarios enabling us to understand and predict the effects of additional inputs of nutrients from the basins to the coastal zone and for the development of strategies for the management and remediation of environmental impacts caused by excessive nutrient concentrations.

Acknowledgments

This study is part of the National Institute of Science and Technology's Continent-Ocean Transfer of Materials Project, funded by CNPq (Process No. 573.601/2008-9).

References

Brazilian Association of Public Cleaning and Special Waste – ABRELPE, 2011. Outlook of Solid Waste in Brazil. Available: http://www.abrelpe.org.br/panorama_apresentacao.cfm.

National Water Agency – ANA. Overview of the Quality of Surface Waters of Brazil:. Brasília: ANA, 2012.264 p.; il Available: http://pnqa.ana.gov.br/default.aspx.

Andersen, J.H., Schlüter, L., Aertebjerb, G., 2006. Coastal eutrophication: recent developments in definitions and implications for monitoring strategies. J. Plankton Res. 28 (7), 621–628. http://dx.doi.org/10.1093/plankt/fbl001.

Aneja, V.P., Blunden, J., James, K., Schlesinger, W.H., Knighton, R., Gilliam, W., Jennings, G., Niyogi, D., Cole, s, 2008. Ammonia assessment from agriculture: U.S. status and needs. J. Environ. Qual. 37, 515–520. http://dx.doi.org/10.2134/jeq2007.0002in.

Barbosa, J.E.L., Medeiros, E.S.F., Brasil, J., Cordeiro, R.S., Crispim, M.C.B., Silva, G.H.G., 2012. Aquatic systems in semi-arid Brazil: limnology and management. Acta Limnol. Bras. 24 (1), 103–118. http://dx.doi.org/10.1590/S2179-975X2012005000030.

Battye, W., Aneja, V.P., Roelle, P.A., 2003. Evaluation and improvement of ammonia emissions inventories. Atmos. Environ. 37 (27), 3873–3883. http://dx.doi.org/10.1016/S1352-2310(03)00343-1.

Boyer, E.W., Goodale, C.L., Jaworski, N.A., Howarth, R.W., 2002. Anthropogenic nitrogen sources and relationships to riverine export in the northeastern USA. Biogeochemistry 57/58, 137–169. http://dx.doi.org/10.1023/A:1015709302073.

Brady, N.C., Weil, R.R., 1996. The Nature and Properties of Soils, 11 ed. Prentice Hall, New Jersey.

Bredemeier, C., Mundstock, C.M., 2000. Regulação da absorção e assimilação do nitrogênio nas plantas. Ciência Rural Santa Maria. ISSN: 0103-8478 30 (2), 365–372.

Cantarella, H., 2007. Nitrogen. In: Novaes, R.F., Alvarez, V.H., Barros, N.F., Fontes, R.L.F., Cantarutti, R.B., Neves, J.C.L. (Eds.), Soil Fertility. Brazilian Society of Soil Science, Viçosa, MG, pp. 276–374.

Caraco, N.F., Cole, J.J., 1999. Human impact on nitrate export: an analysis using major world rivers. Ambio 28, 167–170.

Development Company of the Valley of the São Francisco and Parnaíba – CODEVASF, 2006. Action Plan for Integrated Development of the Parnaíba Basin, PLANAP: Final Report: Strategic Action Plan of the Parnaíba Basin. TDA Desenho & Arte Ltda, Brasília, DF, p. 130 il. Available: http://www.codevasf.gov.br/.

Cunha, P.E.V., 2010. Emission Factors – Nutrients and Heavy Metals – Shrimp Farm Effluent into the Estuary of the River Potengi/RN – Brazil. School of Engineering of São Carlos, University of São Paulo. Doctoral thesis. Available: http://www.teses.usp.br/teses/disponiveis/18/18138/tde-02062010-093706/publico/paulo_cunha.pdf.

Cunha, D.G.F., Bottino, F., Calijuri, M.C., 2010. Land use influence on eutrophication-related water variables: case study of tropical rivers with different degrees of anthropogenic interference. Acta Limnol. Bras. 22 (1), 35–45. http://dx.doi.org/10.4322/actalb.02201005.

European Environment Agency – EEA, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 Establishing a Framework for Community Action in the Field of Water Policy as Amended by Decision 2455/2001/EC and Directives 2008/32/EC, 2008/105/EC and 2009/31/EC. Available: http://www.europarl.europa.eu/.

Brazilian Company for Agriculture and Livestock – EMBRAPA, 2004. Technologies for waste management in swine production: manual of good practices/Coordinated by Paulo Armando Victoria de Oliveira. Embrapa Swine and Poultry, Concordia, p. 109, 29cm. Available: http://www.cnpsa.embrapa.br/pnma/pdf_doc/doc_pnma.pdf.

Brazilian Company for Agriculture and Livestock – EMBRAPA, 2003. Liming and Fertilization in No-tillage System in Cerrado/Carlos Alberto Campos Bernardi. [et al.]. Embrapa Solos, Rio de Janeiro, p. 22 (Embrapa Soils. Documents; n. 46). http://www.ipipotash.org/pdf/countrysp/documentos46.pdf.

Brazilian Company for Agriculture and Livestock – EMBRAPA, 2009. Fertilizing for High Yield and Quality: Tropical Fruits of Brazil/Coordinated by Lindbergue Araújo Crisóstomo. EMBRAPA Tropical Agroindustry, Alexey Naumov – Fortaleza, 238 p.; 21 cm. Available: http://www.ipipotash.org/udocs/IPI_Bulletin_18_Tropical_Fruits.pdf.

Food and Agriculture Organization of United Nations – FAO, 2012. Animal Feed Resources Information System (AFRIS). Manure. Available: http://www.fao.org/ag/AGA/AGAP/FRG/AFRIS/Data/476.HTM. acessado em 20 de novembro de 2012.

Faulkner, W.B., Shaw, B.W., 2008. Review of ammonia emission factors for United States animal agriculture. Atmos. Environ. 42, 6567. http://dx.doi.org/10.1016/j.atmosenv.2008.04.021.

Filoso, S., Martinelli, L.A., Howarth, R.W., Boyer, E.W., Dentener, F., 2006. Human activities changing the nitrogen cycle in Brazil. Biogeochemistry 79 (1–2), 61–89. http://dx.doi.org/10.1007/s10533-006-9003-0.

Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., 2003. The nitrogen cascade. BioScience 53 (4.), 341–356. http://www.jstor.org/stable/1314367.

Galvão, S.R.S., Salcedo, I.H., Oliveira, F.F., 2008. Nutrient build up in sandy soils receiving manure additions. Pesq. Agropec. Bras. 43, 99–105. http://dx.doi.org/10.1590/S0100-204X2008000100013.

Golley, F.B., Mc Guiness, J.T., Clements, R.G., Child, G.I., Duever, M.J., 1978. Mineral cycling in a Tropical Rainforest Ecosystem. EDUSP, São Paulo.

Goudie, A., 1987. The Human Impact: on the Natural Environment. MIT Press Ed, Cambridge, Massachusetts.

Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), 1999. Methods of Seawater Analysis, third. ed. Verlag Chemie, Weinheim, p. 419. cap. 10. http://dx.doi.org/10.1002/9783527613984.

Green, P., Vörösmarty, C.J., Meybeck, M., Galloway, J., Peterson, B., Boyer, E., 2004. Pre-industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on typology. Biogeochemistry 68, 71–105. http://dx.doi.org/10.1023/B:BIOG.0000025742.82155.92.

Greenland, D.J., Lal, R., 1977. Soil Conservation and Management in the Humid Tropics. Willey, Chischester. http://dx.doi.org/10.1002/esp.3290040110.

Hadas, A., Agassi, M., Zhevelev, H., Kautsky, L., Levy, G.J., Fizik, E., Gotessman, M., 2004. Mulching with composted municipal solid wates in Central Negev, Israel II. Effect on available nitrogen and phosphorus and organic matter in soil. Soil Tillage Res. 78, 115–128. http://dx.doi.org/10.1016/j.still.2004.02.020.

Hjelmar, O., Andersen, L., Hansen, J.B., VKI Denmark, 2000. Leachate Emissions from Landfills. Final Report. Swedish Environmental Protection Agency, Stockholm, Sweden. Available: http://swedishepa.se/Documents/publikationer/afr-r-265-se.pdf.

Howarth, R.W., 2008. Coastal nitrogen pollution: a review of sources and trends globally and regionally. Harmful Algae 8 (1), 14–20. http://dx.doi.org/10.1016/j.hal.2008.08.015.

Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., Zhao-liang, Zhu, 1996. Regional nitrogen budgets and riverine N and P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35 (1), 75–139. http://dx.doi.org/10.1007/BF02179825.

Brazilian Institute of Geography and Statistics – IBGE, 2012. Survey of Basic Municipal Information. Profile of Brazilian Cities, Rio de Janeiro. ISBN 978-85-

240-4256-2 (CD-ROM). Available: ftp://ftp.ibge.gov.br/Perfil_Municipios/2011/munic2011.pdf.

Intergovernmental Panel on Climate Change (IPCC), 2006. Guidelines for National Greenhouse Gas Inventories. Available: http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.htm.

Jacomine, P.K.T., Cavalcanti, A.C., Pessoa, S.C.P., Burgos, N., Mélo-Filho, H.F.R., Lopes, O.F., Medeiros, L.A.R., 1986. Exploratory Survey – Reconnaissance Soil of the State of Piauí. EMBRAPA-SNLCS/SUDENE -DRN, Rio de Janeiro, p. 782 ilust. Available: http://library.wur.nl/isric/index2.html?url=http://library.wur.nl/WebQuery/isric/11680.

Jickells, T., 2006. The role of air-sea exchange in the marine nitrogen cycle. Biogeosci. Discuss. 3, 183–210. http://dx.doi.org/10.5194/bgd-3-183-2006.

Lacerda, L.D., 2006. Inputs of nitrogen and phosphorus to estuaries of northeastern Brazil from intensive shrimp farming. Braz. J. Aquat. Sci. Technol. 10 (2), 13–27. http://dx.doi.org/10.14210/bjast.v10n2.

Lacerda, L.D., Vaisman, A.G., Maia, L.P., Cunha, E., Silva, C.A.R., 2006. Relative importance of nitrogen and phosphorus emissions from shrimp farming and other anthropogenic sources for six estuaries along the NE Brazilian coast. Aquaculture 253, 433–446. http://dx.doi.org/10.1016/j.aquaculture.2005.09.005.

Lacerda, L.D., Molisani, M.M., Sena, D., Maia, L.P., 2008. Estimating the importance of natural and anthropogenic sources on N and P emission to estuaries along Ceará State Coast NE Brazil. Environ. Monit. Assess. 141, 149–164. http://dx.doi.org/10.1007/s10661-007-9884-y.

Malavolta, E., Dantas, J.P., 1980. Nutrition and fertilization of corn. In: Paterniani, E. (Ed.), Maize Breeding and Production in Brazil, 2° ed. Fundação Cargill, São Paulo, pp. 429–479.

Marins, R.V., Paula-Filho, F.J., Eschrique, S.A., Lacerda, L.D., 2011. Anthropogenic sources and distribution of phosphorus in sediments from the Jaguaribe River estuary, NE. Brazil. Braz. J. Biol. 71 (3), 673–678. http://dx.doi.org/10.1590/S1519-69842011000400011.

Martinelli, L.A., Coletta, L.D., Ravagnani, E.C., Camargo, P.B., Ometto, J.P.H.B., Filoso, S., Victoria, R.L., 2010. Dissolved nitrogen in rivers: comparing pristine and impacted regions of Brazil. Braz. J. Biol. 70 (3 Suppl), 709–722. http://dx.doi.org/10.1590/S1519-69842010000400003.

Mello, W.Z., Almeida, M.D., 2004. Rainwater chemistry at the summit and southern flank of the Itatiaia massif, Southeastern Brazil. Environ. Pollut. 129 (1), 63–68. http://dx.doi.org/10.1016/j.envpol.2003.09.026.

Mesquista, B.F., Barreto, R., 2011. Monitoring of shrimp farming activity in the areas of mangrove APA Delta of between 2005 and 2009. In: XV Brazilian Symposium on Remote Sensing. – SBSR, Curitiba, PR, Brazil, May, 2011. INPE, p. 2044.

Meybeck, M., Dürr, H.H., Vörösmarty, C.J., 2006. Global coastal segmentation and its river catchment contributors: a new look at land-ocean linkage. Glob. Biogeochem. Cycles 20, GB1S90. http://dx.doi.org/10.1029/2005GB002540.

Mikkelsen, R., 2009. Ammonia emissions from agricultural operations: fertilizer. Better Crops 93 (4), 9–11. Available: http://www.ipni.net/bettercrops.

Mizerkowski, B.D., Hesse, K., Ladwig, N., Machado, C., Rosa, R., Araujo, T., Koch, D., 2012. Sources, loads and dispersion of dissolved inorganic nutrients in Paranaguá Bay. Ocean Dyn. 62, 1409–1424. http://dx.doi.org/10.1007/s10236-012-0569-x.

Ministry of Environment of Brazil – MMA, 2006. Notebook Hydrographic Region Parnaíba/Ministry of Environment, Department of Water Resources – SRH. MMA, Brasília, p. 184 il. color.; 27cm.

Molisani, M.M., Esteves, F.A., Lacerda, L.D., Rezende, C.E., 2013. Natural and anthropogenic emissions of nitrogen, phosphorus and metals for the Macaé River basin (Macaé, RJ, Brazil) under the influence of exploration of oil and gas in the Campos Basin. Quím. Nova 36 (1), 27–66. http://dx.doi.org/10.1590/S0100-40422013000100006.

Mota, F.S.B., Von Sperling, M., 2009. Research Program on Basic Sanitation – PROSAB. In: Sewage Nutrients: Use and Removal, vol. 2. ABES, Rio de Janeiro, 428 p.: il. Available: http://www.finep.gov.br/prosab/livros/prosab5_tema%202.pdf.

Müller, R., Wiedemann, O., 1955. Die Bestimmung des Nitrat-Ions in Wasser. Von Wasser, vol. 22, p. 247.

Noriega, C., Araujo, M., 2009. Nitrogen and phosphorus loading in coastal watersheds in northeastern Brazil. J. Coast. Res. SI 56 (Proceedings of the 10th International Coastal Symposium), 871–875. Lisbon, Portugal, ISSN 0749-0258 Available: http://e-geo.fcsh.unl.pt/ICS2009/_docs/ICS2009_Volume_I/871.875_C.Noriega_ICS2009.pdf.

Novais, R.F., Smyth, T.J., Nunes, F.N., 2007. Phosphorus. In: Novaes, R.F., Alvarez, V.H., Barros, N.F., Fontes, R.L.F., Cantarutti, R.B., Neves, J.C.L. (Eds.), Soil Fertility. Brazilian Society of Soil Science, Viçosa, MG, pp. 276–374.

National Research Council – NRC, 2000. Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution. National Academy Press, Washington, DC. Available: http://www.nap.edu/openbook.php?isbn=0309069483.

Oishi, M.K., 1996. Characterization of the Physical Environment, the Physical and Chemical Characteristics and Nutrient Flow in Tributaries of the Watershed of the Barra Bonita Reservoir (Middle Tietê, SP) (Thesis). USP, São Carlos, p. 199.

Paerl, H.W., 2009. Controlling eutrophication along the freshwater–marine continuum: dual nutrient (N and P) reductions are essential. Estuaries Coasts 32 (4), 593–601. http://dx.doi.org/10.1007/s12237-009-9158-8.

Paula, F.C.F., Lacerda, L.D., Marins, R.V., Aguiar, J.E., Ovalle, A.R.C., Falcão Filho, C.A.T., 2010. Natural and anthropogenic emissions of metals and nutrients to the lower contas river basin, Bahia state, Brazil. Quím. Nova 33 (1), 70–75. http://dx.doi.org/10.1590/S0100-40422010000100014.

De Paula Filho, F.J., Marins, R.V., Lacerda, L.D., Aguiar, J.E., Perez, T.F., 2015. Background values for evaluation of heavy metal contamination in sediments in the Parnaíba River Delta estuary, NE/Brazil. Mar. Pollut. Bull. http://dx.doi.org/10.1016/j.marpolbul.2014.08.022.

Paula Filho, F.J., de Moura, M.C.S., Marins, R.V., 2012. Phosphorus geochemical fractioning in water and sediment from Corrente River, Catchment, Parnaíba/PI. Rev. Virtual Quím. 4 (6), 623–640.

Reddy, K.R., Kadlec, R.H., Flaig, E., Gale, P.M., 1999. Phosphorus retention in streams and wetlands: a review. Crit. Rev. Environ. Sci. Technol. 29 (1), 83–146. http://dx.doi.org/10.1080/10643389991259182.

Salomons, W., 2004. European Catchments: Catchment Changes and Their Impact on the Coast. Institute for Environmental Studies. Vrije Universiteit, Amsterdam, ISBN 90 5383 923 2, p. 61.

Sampaio, Y., Costa, E.F., Albuquerque, E., Sampaio, B.R., 2008. Socio-economic impacts of shrimp farming Navy in selected municipalities Northeast Brazil. Rev. Econ. Sociol. Rural. 46 (4), 1015–1042. http://dx.doi.org/10.1590/S0103-20032008000400005.

Schlesinger, W.H., 1997. Biogeochemistry: an Analysis of Global Change. Academic Press, San Diego.

Schlesinger, W., Hartley, A., 1992. A global budget for atmospheric NH_3. Biogeochemistry 15 (3), 191–211. http://dx.doi.org/10.1007/BF00002936.

Seitzinger, S.P., Harrison, J.A., Dumont, E., Beusen, A.H.W., Bouwman, A.F., 2005. Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: an overview of Global Nutrient Export from Watersheds (NEWS) models and their application. Glob. Biogeochem. Cycles 19, GB4S01. http://dx.doi.org/10.1029/2005GB002606.

Seitzinger, S.P., Mayorga, E., Bouwman, A.F., Kroeze, C., Beusen, A.H.W., Billen, G., Van Drecht, G., Dumont, E., Fekete, B.M., Garnier, J., Harrison, J.A., 2010. Global river nutrient export: a scenario analysis of past and future trends. Glob. Biogeochem. Cycles 24 (4) n/a–n/a. http://dx.doi.org/10.1029/2009GB003587.

Silva, L.F., 1996. Tropical Soils: Aspects Pedological, Ecological and Management. Terra Brasilis Editora, São Paulo.

Smil, V., 2000. Phosphorus in the environment: natural flows and human interferences. Annu. Rev. Energy Environ. 25, 53–88. http://dx.doi.org/10.1146/annurev.energy.25.1.53.

National Secretary of Environmental Sanitation – SNSA, 2012. National Information System on Sanitation: Diagnosis of Water Services and Sewage –2010. MCIDADES.SNSA, Brasília. Available: http://www.snis.gov.br/PaginaCarrega.php?EWRErterterTERTer=95.

Tam, N.F.Y., Wong, Y.S., 1996. Retention of wastewater-borne nitrogen and phosphorus in mangrove soils. Environ. Technol. 17 (8), 851–859. http://dx.doi.org/10.1080/09593331708616453.

Thomas, Y., Courties, C., El, Y., Herbland, A., Lemonnier, H., 2010. Spatial and temporal extension of eutrophication associated with shrimp farm wastewater discharges in the New Caledonia lagoon. Mar. Pollut. Bull. 61 (7–12), 387–398. http://dx.doi.org/10.1016/j.marpolbul.2010.07.005.

U.S. Environmental Protection Agency – USEPA, 2003. National Management Measures to Control Nonpoint Source Pollution from Agriculture. EPA. 841-B-03-004. Available: http://water.epa.gov/polwaste/nps/agriculture/agmm_index.cfm.

U.S. Geological Survey – USGS, 2011. SPARROW Surface Water-quality Modeling. Available: http://water.usgs.gov/nawqa/sparrow/index.html.

Valderrama, J.C., 1981. The simultaneous analisys of total nitrogen and phosphorus in natural waters. Mar. Chem. 10, 109–122. http://dx.doi.org/10.1016/0304-4203(81)90027-X.

Vasconcelos, J.F., Barbosa, J.E.L., Diniz, C.R., Ceballos, B.S.O., 2011. Cyanobacteria in reservoirs in the state of Paraíba: occurrence, toxicity and regulatory factors. Bull. Braz. Soc. Limnol. 39 (2), 1–20. Available: http://www.ablimno.org.br/boletins/pdf/bol_39(2-2).pdf.

Viero, F., Bayer, C., Fontoura, S.M.V., Moraes, R.P., 2014. Ammonia volatilization from nitrogen fertilizers in no-till wheat and maize in southern Brazil. Rev. Bras. Ciênc. Solo. ISSN: 0100-0683 38 (5), 1515–1525. http://dx.doi.org/10.1590/S0100-06832014000500017.

Vlek, P.L.G., Byrnes, B.H., 1986. The efficacy and loss of fertilizer N in lowland rice. Fertil. Res. 9, 131–147. http://dx.doi.org/10.1007/BF01048699.