Anais da Academia Brasileira de Ciências (2012) 84(4): 919-930
(Annals of the Brazilian Academy of Sciences)
Printed version ISSN 0001-3765 / Online version ISSN 1678-2690
www.scielo.br/aabc

# Influence of land use changes on water chemistry in streams in the State of São Paulo, southeast Brazil

**DANIELA M.L. SILVA**[1], **PLÍNIO B. CAMARGO**[2], **WILLIAM H. MCDOWELL**[3],
**IVAN VIEIRA**[2], **MARCOS S.M.B. SALOMÃO**[4] **and LUIZ A. MARTINELLI**[2]

[1]Universidade Estadual de Santa Cruz, Departamento de Ciências Biológicas,
Rodovia Ilhéus – Itabuna, Km 16, 45662-900 Ilhéus, BA, Brasil
[2]Centro de Energia Nuclear na Agricultura, Universidade de São Paulo,
Av. Centenário, 303, Caixa Postal 96, 13416-000 Piracicaba, SP, Brasil
[3]Department of Natural Resources, University of New Hampshire, 05 Main Street, Durham, NH 03824, USA
[4]Universidade Estadual do Norte Fluminense Darcy Ribeiro, Centro de Biociências e Biotecnologia,
Av. Alberto Lamego, 2000, 28013-600 Campos dos Goytacazes, RJ, Brasil

*Manuscript received on May 31, 2011; accepted for publication on April 24, 2012*

## ABSTRACT

Streamwater is affected by several processes in the watershed including anthropogenic activities that result in changes in water quality as well as in the functioning of these stream ecosystems. Therefore, this work aims to evaluate the concentration of major ions ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $NH_4^+$, $NO_3^-$, $NO_2^-$, $Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$, $HCO_3^-$) in streams in the state of São Paulo (southeast Brazil). The sampling sites are located at undisturbed (ombrophilus dense forest, semideciduous forest and savanna – *cerrado*) and disturbed areas (pasture, urbanization and sugar cane crops). Streamwater chemistry varied according to land use change and, in general, was higher in disturbed sites. Streams located in undisturbed sites at Ribeira de Iguape/Alto Paranapanema watershed (streams 1, 2 and 3) seem to be regulated by soil characteristics, as the disturbed streams located at the same watershed covered by pasture (stream 7) showed high concentration for the most of the variables. Exception to streams located at Pontal do Paranapanema watershed where both disturbed (stream 8) and undisturbed streams (stream 4 and 5) presented similar patterns for almost all variables measured.

**Key words**: hydrochemistry, land use, streams, watersheds.

## INTRODUCTION

Anthropogenic activities result in several physical and chemical changes that can alter the structure and functioning of stream ecosystems (Ohrui and Mitchell 1998, Caraco and Cole 1999, Niyogi et al. 2004). Small catchments represent important means of identifying changes in land use, mainly because they are most effective in processing and transporting elements, such as C and N, as well as, major cations and anions (Likens 2004, Thomas et al. 2004). Water chemistry analysis provides a measure of the health and integrity of the ecosystem since this streamwater represents local and regional hydrosphere and provide certain basic functions of ecosystems (Thomas et al. 2004, Niyogi et al. 2004).

---

Correspondence to: Daniela Mariano Loes da Silva
E-mail: dmlsilva@gmail.com

Streamwater is affected by biotic and abiotic processes in the watershed, including climate, hydrology, soil properties, geomorphology, topography and land use (Ometto et al. 2000, McKee et al. 2001, Likens 2004, Thomas et al. 2004). The effects of various processes on stream chemistry have been intensively studied in many forested watersheds in temperate regions. Changes in land use involve physical and chemical alterations such as increased light, nitrate, chloride and sulfate. These effects include reduced uptake by vegetation that change soil processes such as mineralization and nitrification (Wang et al. 2006). The effects of change in land use on the biogeochemistry have also been described in the literature for both major rivers and streams. It has been shown that these changes affect nitrate, ammonium, calcium, potassium and aluminum concentrations in streams located in temperate (Wang et al. 2006, Kamisako et al. 2008, Rai et al. 2010) and tropical regions (Neill et al. 2006, Andrade et al. 2011, Silva et al. 2011).

Several studies in tropical watersheds evaluated the impact of urbanization and agricultural practices on water quality (Ballester et al. 1999, Neill et al. 2001, Biggs et al. 2004, Martinelli et al. 2008, Salomão et al. 2008, Germer et al. 2009, Andrade et al. 2011). Studies in subcatchments in southeastern and southern Brazil have shown that small streams are severely affected by urbanization and agricultural practices such as pastures, considerably increasing dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) (Daniel et al. 2002, Silva et al. 2008) in addition to several ions such as nitrate, chloride and ammonium (Silva et al. 2008, Germer et al. 2009, Andrade et al. 2011). As a result, the structure of biota communities is affected by these activities, decreasing some species while urbanization increases (Ometto et al. 2000, Ramirez et al. 2009). It has been also recognized that urbanization represents a source of heavy metals (Tomazelli et al. 2003, Guimarães and Sígolo 2008, Campos et al. 2009) and organochlorine compounds (Miguel et al. 2003, Silva et al. 2008).

Since there are few studies of undisturbed streams in Brazil, mainly in the State of São Paulo, this work aims to evaluate the concentration of major ions in streams in this region (southeast Brazil).

## STUDY SITES

The characterization of study sites is described in tables I and II. The sampling sites 1, 2, 3 and 7 are located in the Ribeira de Iguape watershed (A), sites 4, 5 and 8 in the Pontal do Paranapanema watershed, site 6 in the Mogi-Guaçú watershed and sites 9 and 10 in the Piracicaba watershed (Figure 1). The sites 1, 2, 3, 4 and 5 are located at undisturbed areas of the Atlantic forest under two different physiognomies (Ombrophilus Dense and Semi Deciduous forests) and site 6 is located at an area of savanna (Cerrado) in state parks of São Paulo, Brazil. The Ribeirão Grande (site 7), Lageado (site 8), Marins (site 9) and Palmeiras (site 10) streams are located at disturbed areas with distinct land use types (Table II).

Water samples in forested areas were sampled monthly from May 2002 to April 2003 and in deforested areas were sampled six times in this same period.

## METHODS

Abiotic parameters (dissolved oxygen, conductivity, pH and temperature) were measured in the field. Conductivity was measured with an Amber Science 2052 meter, dissolved oxygen and temperature were measured with a Yellow Spring 58 meter and pH with an Orion 250A meter. For chemical analyses, water samples were collected using a Niskin bottle. Samples for major ions ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $NH_4^+$, $NO_3^-$, $NO_2^-$, $Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$) and Dissolved Inorganic Carbon (DIC) were filtered through GF/F filter (0.7 μm) and preserved with thymol (biocide

**TABLE I**

**Study area description.**

| *Study sites* | | *Streams* | *Lat/long* | *Discharge ($m^3s^{-1}$) (min-max)* |
|---|---|---|---|---|
| | | **Undisturbed sites**<br>*State parks* | | |
| Capão Bonito | 1 | Carmo<br>(Ribeira de Iguape/Alto Paranapanema watershed) | 24 ° 17’ 36”<br>48 ° 25’ 05’ | 0.3 – 1.4 |
| Capão Bonito | 2 | Lageado<br>(Ribeira de Iguape/Alto Paranapanema watershed) | 24 ° 17’ 36”<br>48 ° 25’ 05” | 0.2 - 0.54 |
| Capão Bonito | 3 | Mortes<br>(Ribeira de Iguape/Alto Paranapanema watershed) | 24 ° 16’ 02”<br>48 ° 24’ 36” | 0.4 - 2.5 |
| Teodoro Sampaio | 4 | Taquara<br>(Pontal do Paranapanema watershed) | 22 ° 36’ 00”<br>52 ° 14’ 46” | 0.002 - 0.01 |
| Teodoro Sampaio | 5 | Caldeirão<br>(Pontal do Paranapanema watershed) | 22 ° 28’ 32”<br>52 ° 20’ 36” | 0.002 - 0.03 |
| Santa Rita do Passa Quatro | 6 | Paulicéia<br>(Mogi Guaçú watershed) | 21 ° 38’ 58”<br>47 ° 38’ 24” | 0.4-0.6* |
| | | **Disturbed sites** | | |
| Capão Bonito | 7 | Ribeirão Grande<br>(Ribeira de Iguape/Alto Paranapanema watershed) | 24 ° 05’ 41”<br>48 ° 21’ 47” | 0.35 - 0.64 |
| Teodoro Sampaio | 8 | Lageado<br>(Pontal do Paranapanema watershed) | 22 ° 29’ 21”<br>52 ° 11’ 41” | 0.35 - 0.64 |
| Piracicaba | 9 | Marins<br>(Piracicaba watershed) | 22 ° 43’ 20”<br>47 ° 41’ 28” | 0.14 – 0.64** |
| Piracicaba | 10 | Palmeiras<br>(Piracicaba watershed) | 22 ° 43’ 38”<br>47 ° 34’ 00” | - |

* Data from Silva et al. (2007).

** Data from Faganello et al. (2007).

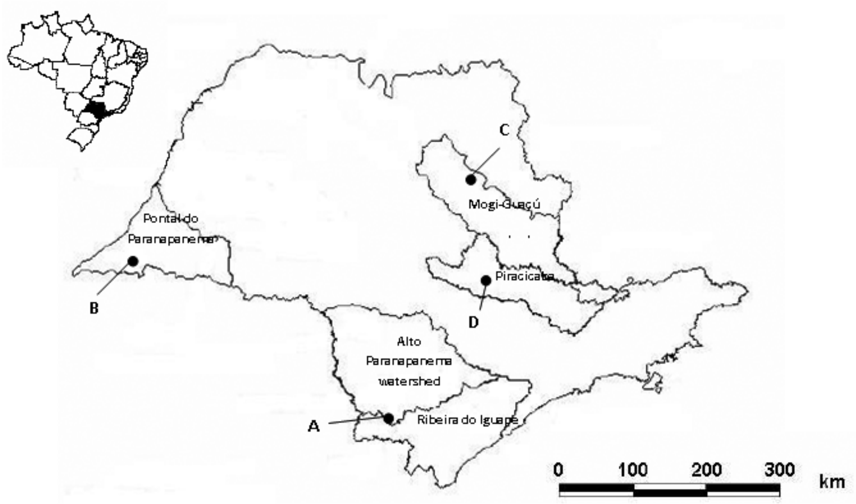

**Figure 1 -** Map of the state of São Paulo showing the sampling sites located at four watersheds. **A**: sites 1, 2, 3 and 7; **B**: sites 4, 5 and 8; **C**: site 6; **D**: site 8 and 9.

– C10H14O). Major ions were analyzed with a DIONEX DX 500 and DIC were determined with a Shimadzu TOC 5000 and the $HCO_3^-$ concentration calculated from measurements of the pH, temperature and DIC concentrations (Butler 1991).

Soil samples were collected at undisturbed streams in the depth of 0-10 cm and the analyses of pH, Organic Matter (OM), P (phosphorus), $K^+$, $Na^{2+}$, $Mg^{2+}$ were realized at ESALQ/USP and N% C:N ratio at Laboratory of Isotopic Ecology at CENA/USP.

Statistical Analyses – The Kolmogorov – Smirnov & Lilliefors test were used to test data distribution. If the D value was not significant a Tukey honest significant difference test (HSS; Post hoc test; $P<0.05$; Statistics 6.0 software) was applied to test for statistically significant differences between watersheds. Most of our data did not follow a normal distribution, therefore, we used the Spearman ranking test to determine correlations among data at $P<0.05$.

**TABLE II**

**Land use types, soil cover and annual precipitation of each sampling sites.**

| Study sites | 1 2 3 | 4 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|
| Land use | Ombrophilus dense forest | Semideciduous forest | Savanna (Cerrado) | 75% Pasture<br>3% urban<br>18% forest<br>4% sugar cane | 90% pasture<br>10% forest | 44% pasture<br>30% sugar cane<br>11% forest<br>8.6% other crops<br>6.4% urban | 90.8% sugar cane<br>3.5% urban<br>3.3% forest<br>1.9% other crops<br>0.6% pasture |
| Soil | Cambisol | latosol | red yellow latosols | Latosol | latosol | latosol | Latosol |
| Annual prec. (mm) | 2,000 | 1,500 | 1,400 | 2,000 | 1,500 | 1,400 | 1,400 |

## RESULTS

Streamwater chemistry varied according to soil characteristics or land use change. In general, the majority of ions in streams, as well as pH, were lower in stream 6 (undisturbed; $P<0.05$) and higher at stream 7 (disturbed; $P<0.05$) (Figure 2). Stream 6 also showed low ionic content, with conductivity values ranging from 5.3 to 6.3 µS $cm^{-1}$ and pH from 5.2 to 5.4. Dissolved oxygen presented distinct values, decreasing according to the decrease of native forest percentage in the watershed. Higher values were found in streams 1, 2, 3 and 7, all located in the same region (Capão Bonito) (Table II) followed by streams 4, 5 with 6, 8, 9 and 10 presenting the lower values (Figure 3). Stream chemistry concentration was dominated by $HCO_3^-$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$ and $Cl^-$ (Table III). Streams located in undisturbed areas presented low values for almost all ions compared to disturbed ones (Table III). The concentration of $Ca^{2+}$ and $Mg^{2+}$ were significantly higher in stream 2 ($P<0.05$) and 7 (Figure 4). As a result, the conductivity and $HCO_3^-$ concentrations were also higher, both results also coincides with soil characteristics since that cambisoils showed the higher concentrations to $K^+$, $Ca^{2+}$ and $Mg^{2+}$ (Table IV).

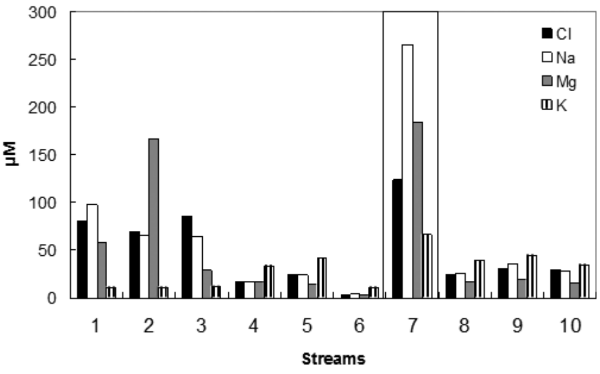

**Figure 2 -** Concentration of Cl- (chloride), $Na^+$ (sodium), $Mg^{2+}$ (magnesium), $K^+$ (potassium) of streamwater sample collected at undisturbed (1, 2, 3, 4, 5, 6) and disturbed sites (7, 8, 9, 10) (µM).

**TABLE III**

**Comparision of mean concentration of conductivity (Cond); dissolved oxygen (DO), $HCO_3^-$, $Na^+$, $Mg^{2+}$, $K^+$, $Ca^{2+}$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $PO_4^{3-}$ between tropical watersheds with different land uses. Cond (µS.cm $^{-1}$); ions (µM.L$^{-1}$).**

| Streams | pH | Cond | DO | Cl | $HCO_3^-$ | $SO_4^{2-}$ | $NO_3^-$ | $PO4^{3-}$ | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | µS.cm$^{-1}$ | Mg.L-1 | | | | | µM | | | | | |
| **Undisturbed sites**<br>*located at state parks* | | | | | | | | | | | | | |
| **1** (n=12) | 7 ± 0 | 38 ± 1 | 10 ± 1 | 81 ± 5 | 173 ± 61 | 9 ± 13 | 22 ± 3 | <0.5 | 98 ± 10 | <3 | 11 ± 4 | 58 ± 10 | 61 ± 12 |
| **2** (n=12) | 7 ± 0 | 35 ± 3 | 9 ± 1 | 85 ± 12 | 136 ± 38 | 22 ± 11 | 24 ± 4 | <0.5 | 64 ± 31 | <3 | 12 ± 6 | 30 ± 13 | 44 ± 19 |
| **3** (n=12) | 8 ± 1 | 162 ± 50 | 10 ± 1 | 70 ± 21 | 1650 ± 79 | 21 ± 22 | 23 ± 8 | 1 | 65 ± 10 | <3 | 11 ± 3 | 167 ± 42 | 623 ± 236 |
| **4** (n=12) | 6 ± 0 | 20 ± 6 | 8 ± 1 | 17 ± 6 | 55 ± 12 | 4 ± 2 | 6 ± 1 | 3 ± 1 | 18 ± 5 | <3 | 34 ± 11 | 17 ± 5 | 34 ± 10 |
| **5** (n=12) | 6 ± 0 | 26 ± 5 | 8 ± 1 | 25 ± 9 | 79 ± 18 | 1 ± 1 | 13 ± 1 | 3 ± 1 | 24 ± 7 | <3 | 41 ± 17 | 14 ± 4 | 44 ± 12 |
| **6** (n=12) | 5 ± 0 | 6 ± 1 | 7 ± 0 | 4 ± 2 | 3 ± 2 | 1 ± 1 | 2 ± 0 | <0.5 | 5 ± 2 | <3 | 11 ± 9 | 3 ± 1 | 9 ± 5 |
| **Disturbed sites** | | | | | | | | | | | | | |
| **7** (n=11) | 8 ± 0 | 125 ± 10 | 9 ± 1 | 124 ± 42 | 1089 ± 84 | 11 ± 8 | 21 ± 4 | <0.5 | 265 ± 68 | <3 | 66 ± 41 | 185 ± 37 | 308 ± 87 |
| **8** (n=10) | 6 ± 0 | 20 ± 1 | 7 ± 0 | 24 ± 3 | 50 ± 17 | 1 ± 1 | 18 ± 5 | <0.5 | 26 ± 2 | <3 | 39 ± 3 | 18 ± 2 | 31 ± 8 |
| **9** (n=2) | 8 ± 0 | 306 ± 37 | 7 ± 1 | 30 ± 0 | 2502 ± 128 | 1 ± 0 | 11 ± 0 | 1 ± 0 | 35 ± 2 | <3 | 44 ± 1 | 20 ± 1 | 45 ± 2 |
| **10** (n=2) | 7 ± 0 | 214 ± 23 | 7 ± 0 | 30 ± 0 | 695 ± 22 | 0 ± 0 | 12 ± 1 | 1 ± 0 | 28 ± 14 | <3 | 35 ± 15 | 15 ± 7 | 33 ± 17 |

On the other hand, $SO_4^{2-}$, $Na^+$ and $Cl^-$ concentrations were significantly higher in sites 1, 2, 3 and 7 ($P<0.05$). Conductivity and $HCO_3^-$ also presented higher values in streams 3, 7, 9 and 10 ($P<0.05$), the exception was observed in site 8, that presented values similar to undisturbed sites. The ion $NO_3^-$ , as well as, the ion $SO_4^{2-}$ followed the same trend with higher values found in streams 1, 2 and 3 (undisturbed) followed by streams 7 and 8 (disturbed). Chloride presented higher concentrations in undisturbed streams (1, 2 and 3), although the higher concentration was found in stream 7 (125µM; $P<0.05$) (Table III). On the other hand, $PO_4^{3-}$ and $K^+$ showed different patterns in undisturbed sites, with high concentrations in streams 4 and 5 (Table III) in undisturbed areas, and 7 and 10 in disturbed areas. Phosphate in the majority of undisturbed sites (1 to 6) did not surpass the detection limits of 0.53 µM, whereas in disturbed watersheds it ranged from 0.92 to 1.21 µM. The same pattern of concentration was found for $NH_4^+$, which presented all values above the detection limits (<3µM).

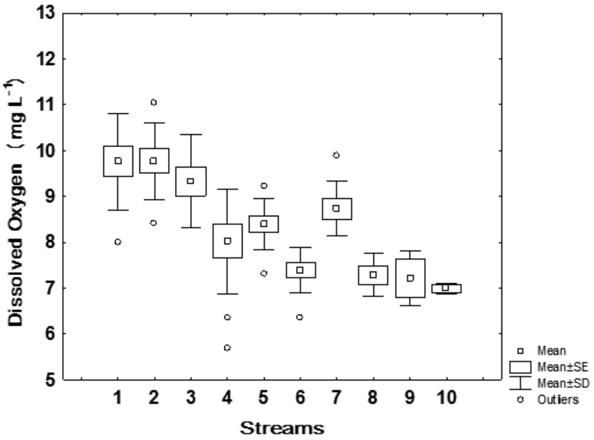

**Figure 3 -** Dissolved oxygen concentration (mg.L$^{-1}$) measures at undisturbed (1, 2, 3, 4, 5, 6) and disturbed sites (7, 8, 9, 10).

**TABLE IV**
**Soil characteristics of watersheds 1, 2, 3, 4, 5 and 6 (O.M.=organic matter; P=phosphorus; SB=sum of bases; Hum= humidity).**

| Watershed | pH | O.M. | P | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | H+Al | SB | T | N | C:N | Hum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $CaCl_2$ | **$g.dm^{-3}$** | $mg.dm^{-3}$ | **$Mmol.dm^{-3}$** | | | | | | % | | % |
| **1** | 4 | 47 | 12 | 2 | 7 | 6 | 83 | 14 | 98 | 0.3 | 9.5 | 35.2 |
| **2/3** | 4 | 52 | 12 | 1 | 27 | 11 | 83 | 39 | 122 | 0.3 | 10.8 | 27.9 |
| **4** | 5 | 22 | 9 | 0.4 | 10 | 4 | 17 | 15 | 31 | 0.1 | 10.2 | 3.9 |
| **5** | 4 | 22 | 9 | 0.4 | 10 | 4 | 20 | 14 | 34 | 0.1 | 11.3 | 4.1 |
| **6** | 4 | 35 | 16 | 0.4 | 4 | 3 | 67 | 8 | 75 | 0.1 | 12.7 | 8.9 |

## DISCUSSION

### STREAMWATER CHEMISTRY

In general, streamwater chemistry was higher in disturbed sites. Several studies reported the impact of land use effect on streams, both in temperate and tropical watersheds (Kamisako et al. 2008, Rai et al. 2010, Andrade et al. 2011, Silva et al. 2011). Streams located in undisturbed sites were reported to be more affected by soil characteristics and precipitation, although the streams located in disturbed areas were affected by different sources according to the land use. For example, Silva et al. (2011) and Germer et al. (2009) reported in Amazonian streams higher nutrients export ($NO_3^-$, $PO_4^{3+}$, $K^+$ and $Mg^{2+}$) in pastures watersheds compared to forest watersheds. Same trend were found by Silva et al. (2007) that found higher concentrations of inorganic nitrogen and carbon in sugar cane crops compared to silviculture and savanna.

It seems that dissolved oxygen reflected the differences in environmental characteristics more than land use. However, dissolved oxygen presents positive correlation only with forests catchments (Spearman correlation r= 0.35; P<0,05 - Table V). Streams 1, 2 and 3 (Capão Bonito) present rapid currents due the presence of a rock river bed, although streams 4, 5 (Teodoro Sampaio) and 6 (Santa Rita do Passa Quatro) present a sandy river bed with a slow current. Therefore, the concentration of dissolved oxygen was higher in streams located in Capão Bonito followed by streams in Teodoro Sampaio and Piracicaba and Santa Rita do Passa Quatro (Figure 3). The values found in stream 6 (located at Santa Rita do Passa Quatro) were lower if compared to other streams in state parks since this area is located under savanna region with presents highly weathered soils and poor nutrient concentrations (Markewitz et al. 2006) that reflected in all parameters of water chemistry evaluated in this work (see above). Silva et al. (2007) evaluating undisturbed stream in this area reported that land use changes such as sugar cane and eucalyptus contribute to a decrease of physicochemical conditions in savanna watersheds.

Conductivity values differed for disturbed and undisturbed sites. It was expected that streams located in disturbed sites would present higher values of conductivity, mainly because of the higher concentrations of several ions. This is true only for streams 7, 9 and 10. Stream 8 did not follow this pattern, presenting similar values of stream 4 and 5, which are located in the same area (Teodoro Sampaio/SP). This watershed is covered mainly by pasture (90%, Table II) and is near an interstate highway. However, it seems that little differences in ion concentrations were affected by these disturbances, probably due the fact that the sites collects were located before the highway.

At the same time, stream 3 is an exception, but in this case, the higher values were found to be due to the higher concentrations of $Ca^{2+}$ and $Mg^{2+}$ in these same streams. These cations were found in higher concentrations in soil samples collected in these watersheds (Table IV). Therefore, it could be inferred that soil characteristics are the main factor affecting the $Ca^{2+}$, $Mg^{2+}$ and, consequently, the conductivity values in stream 3.

The concentration of sodium and chloride found in streams 1, 2 and 3 could be due precipitation inputs since this area is near the coast, and its dry and wet climate could be the main factor affecting these concentrations. These results coincide with ionic concentration evaluated in rainwater in the same study areas that found higher concentrations of these ions also in Capão Bonito (V.P.S. Almeida, unpublished data).

Since most cities in Brazil have no sewage treatment and untreated waste is dumped directly into rivers, high concentrations of several ions were expected. Stream 7 was characterized by high concentrations of several ions, such as Cl-, $K^+$, $Ca^{2+}$ and $Mg^{2+}$, and despite the fact that this stream is probably influenced by precipitation inputs since it is located in the same area as streams 1, 2 and 3, the higher concentrations area probably due to urbanization. This sampling site was located near a small village where the sewage was freely dumped in the stream; therefore, we hypotheses that this sewage significantly contributed with major ions such as Cl-, $Na^+$ and $Mg^{2+}$ (Table V and Figure 2) ($P<0.05$). It is well recognized that the concentration of these ions is severely affected by sewage. In the Piracicaba River basin, the sewage added to these river showed an increase in concentration of $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$ and Cl- (Martinelli et al. 2008). At the same time, $Ca^{2+}$, $Mg^{2+}$ and $HCO_3^-$ presented positive correlations with pasture and perennial cultures in watersheds with different degrees of disturbances in the state of São Paulo, although $Cl^-$ were correlated with urbanization and sugar cane crops (Salomão et al. 2008). Urbanization is also the main land use change that drives the concentrations of almost all major ions in streams in the southeastern of São Paulo if compared to pristine streams at the same area. The higher concentrations of nutrients and major ions were found in streams located at urban areas (Andrade et al. 2011).

On the other hand, potassium presented different patterns for undisturbed streams, with higher concentrations found in streams 4 and 5 covered by semideciduous forest. Dry and wet deposition could be the main factor affecting the concentration of $K^+$ in semi deciduous seasonal forest. The same trend was observed in wet deposition in this area with values 1 to 3 times higher compared to the other watersheds. However, the higher values of potassium were found in disturbed sites, with stream 7 also presenting the highest value of 66 μM, probably due to the domestic sewage and pasture. Pasture represents one of the main land covers affecting the potassium concentration at Turvo, Aguapeí and Piracicaba Rivers in the state of São Paulo, with percentages varying from 44% to 70% in Piracicaba and Aguapeí, respectively (Martinelli et al 2008, Salomão et al. 2008). This vegetation cover decrease the soil permeability, increasing the ion fluxes to streams (Germer et al. 2009) and this seems to be the case of undisturbed streams 1, 2 and 3 and disturbed stream 7 where pasture represents 75% of the watershed.

### NITRATE AND MAJOR CATIONS CONCENTRATIONS

Higher concentrations of $NO_3^-$ were found in streams 1, 2 and 3 located in ombrophilus dense forests when compared to the other streams located in disturbed areas. This is probably due to the soil characteristics and the oxygen availability in these streams (Fig. 4). These sites showed the higher concentration of total nitrogen (three times higher than the other watersheds) and inorganic nitrogen (Table IV). It is associated with higher nitrification and mineralization rates that contributed to an increase of nitrogen leaching. This positive correlation has been also demonstrated in watersheds located in

**TABLE V**

**Spearmans correlation matrix of land use and variables analyzed. Coefficients in bold are significant in P<0.05.**

| | T | pH | DO | Cond | $Cl^-$ | $NO_2^-$ | $SO_4^{2-}$ | $NO_3^-$ | $PO_4^{-3}$ | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $HCO_3^-$ | Forest | Urban | Sugar Cane | Pasture | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **T** | | | | | | | | | | | | | | | | | | | | |
| **pH** | **-0.51** | | | | | | | | | | | | | | | | | | | |
| **DO** | **-0.80** | **0.53** | | | | | | | | | | | | | | | | | | |
| **Cond** | **-0.40** | **0.91** | **0.44** | | | | | | | | | | | | | | | | | |
| **$Cl^-$** | **-0.47** | **0.76** | **0.57** | **0.73** | | | | | | | | | | | | | | | | |
| **$NO_2^-$** | **-0.28** | 0.21 | 0.12 | 0.13 | 0.17 | | | | | | | | | | | | | | | |
| **$SO_4^{2-}$** | **-0.43** | **0.45** | **0.54** | **0.41** | **0.60** | 0.08 | | | | | | | | | | | | | | |
| **$NO_3^-$** | **-0.44** | **0.68** | **0.57** | **0.62** | **0.82** | 0.07 | **0.48** | | | | | | | | | | | | | |
| **$PO_4^{-3}$** | **0.34** | -0.07 | -0.22 | -0.01 | **-0.26** | -0.15 | -0.18 | -0.23 | | | | | | | | | | | | |
| **$Na^+$** | **-0.54** | **0.78** | **0.57** | **0.75** | **0.86** | **0.39** | **0.52** | 0.72 | **-0.26** | | | | | | | | | | | |
| **$NH_4^+$** | 0.06 | -0.12 | -0.12 | -0.19 | -0.08 | **0.26** | -0.05 | 0.04 | 0.06 | -0.06 | | | | | | | | | | |
| **$K^+$** | **0.27** | 0.05 | **-0.31** | 0.10 | 0.05 | 0.18 | -0.13 | -0.08 | **0.52** | 0.12 | 0.07 | | | | | | | | | |
| **$Mg^{2+}$** | **-0.50** | **0.81** | **0.51** | **0.78** | **0.74** | **0.31** | **0.54** | 0.64 | -0.14 | **0.89** | -0.11 | 0.08 | | | | | | | | |
| **$Ca^{2+}$** | **-0.43** | **0.80** | **0.47** | **0.78** | **0.71** | 0.16 | **0.46** | 0.60 | 0.04 | **0.79** | -0.16 | 0.19 | **0.88** | | | | | | | |
| **$HCO_3^-$** | **-0.37** | **0.90** | **0.39** | **0.88** | **0.73** | 0.09 | **0.40** | 0.65 | -0.02 | **0.70** | -0.07 | 0.07 | **0.76** | **0.74** | | | | | | |
| **Forest** | **-0.30** | -0.16 | **0.39** | **-0.25** | -0.17 | -0.18 | 0.21 | -0.07 | 0.06 | -0.21 | -0.13 | **-0.49** | -0.14 | -0.01 | **-0.24** | | | | | |
| **Urban** | 0.08 | **0.40** | -0.20 | **0.51** | **0.35** | **0.26** | -0.01 | 0.05 | 0.05 | **0.35** | -0.04 | **0.48** | **0.29** | 0.23 | **0.48** | **-0.75** | | | | |
| **Sugar Cane** | 0.07 | **0.40** | -0.20 | **0.51** | **0.35** | **0.26** | -0.01 | 0.05 | 0.05 | **0.35** | -0.04 | **0.47** | **0.29** | 0.22 | **0.48** | **-0.75** | **1.00** | | | |
| **Pasture** | **0.25** | 0.17 | **-0.35** | 0.21 | 0.20 | **0.25** | -0.17 | 0.11 | -0.11 | **0.25** | 0.15 | **0.50** | 0.18 | 0.05 | 0.22 | **-0.98** | **0.70** | **0.70** | | |
| **Others** | **0.25** | 0.16 | **-0.32** | **0.39** | -0.02 | -0.17 | **-0.25** | -0.15 | **0.23** | -0.05 | -0.08 | 0.21 | -0.08 | -0.09 | **0.29** | **-0.51** | **0.64** | **0.63** | 0.33 | |

southeast Brazil, with the higher concentrations of nitrate found in sites located in ombrophilus dense forests when compared to sites located in a wetland (Marques et al. 2003).

Nitrate concentration has been reported in several works associated with major cations. According McDowell (2001), tropical forests that are not N limited have high gaseous losses from nitrification, and denitrification and high losses of nitrate in surface run off, resulting in indirect effects such as loss of major cations and decrease in P availability (due to the acidification associated primarily to increased nitrification).

The cations concentration, such as $Ca^{2+}$ and $Mg^{2+}$ that were higher in streams 1 and 2 could be associated with the higher $NO_3^-$ (Figure 5). This association was also confirmed with the spearman analyses that showed positive correlation ($P<0.05$) of $NO_3^-$ with $Na^+$, $Mg^{2+}$, $Ca^{2+}$ and $HCO_3^-$ (Table V). The leaching of this ion from the soil surface mobilizes a cation. As the base cation supply is progressively depleted, the leached cation will either be a proton or mobilized aluminum ion. As this ion is prevalent in tropical soils, aluminum rather than $H^+$ is the dominant cation associated with soil acidity in tropical forests (Jordan 1985, Fenn et al. 1998, Matson et al. 1999).

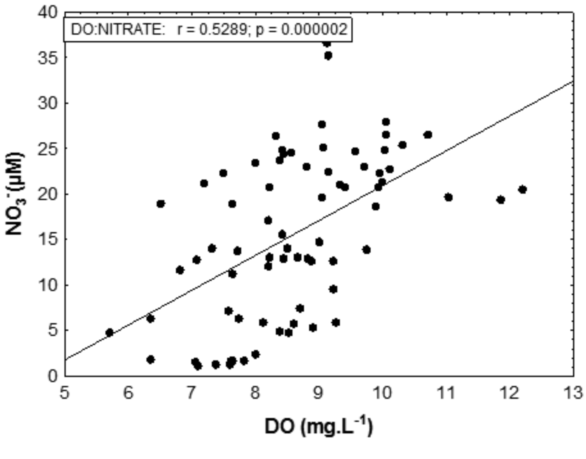

**Figure 4 -** Plot of concentration of dissolved oxygen (DO mg.$L^{-1}$) and nitrate ($NO_3^-$) of streamwater collected at undisturbed (1, 2, 3, 4, 5, 6) and disturbed sites (7, 8, 9, 10).

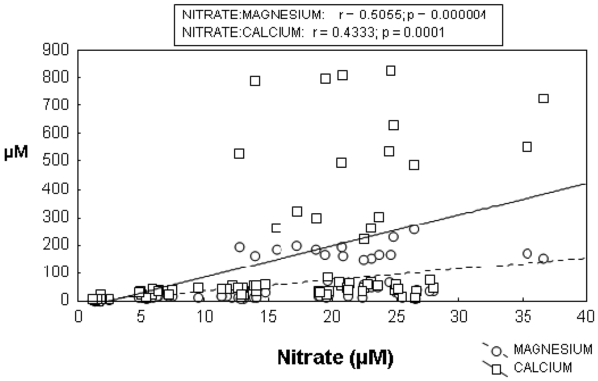

**Figure 5 -** Plot of concentration of nitrate (µM) and magnesium and calcium (µM) of stream water collected at undisturbed (1, 2, 3, 4, 5, 6) and disturbed sites (7, 8, 9, 10).

The higher concentrations of aluminum, calcium and magnesium were found in these soils (streams 1 and 2) (Table IV), and nitrate leaching could represent a link between the N cycle and cation cycles in forest ecosystems, and its concentration could be correlated with $Ca^{2+}$ and Al in stream water (Brujinzel 1992). Losses of $Ca^{2+}$ and Al also have been reported for sites located on inceptisols, which is the predominant soil in 1 and 2. In contrast, sites located in spodsol and oxisol groups (e.g. Amazonian, and streams 4, 5 and 6) exhibit lower losses of calcium and magnesium (Currie et al. 1999). According to Christopher et al. (2006) the relationship between $NO_3^-$ and $Ca^{2+}$ can be explained by differences in tree species and soil properties, and similar to our results they found a positive relationship between these ions.

Some streams draining forested watersheds in Tennessee, USA showed a high export of $Ca^{2+,}$ $Mg^{2+}$ and $HCO_3^-$. However in this case, the area is underlain with dolomites characterized by a high concentration of $CaCO_3$ – (Mulholland 1992). In our case, the bedrock composition is characterized by phyllites recognized to increase the nitrate from streams. According to Holloway et al. (1998), the nitrogen flux in streams through areas dominated by phyllites had an export 100 times higher (19.9 kg.N.$ha^{-1}$.$yr^{-1}$) than streams located in areas dominated by intrusive rocks (0.12 kg.N.ha$^{-1}$.yr$^{-1}$). Despite the fact that N concentration of the rocks in our areas has not been documented, we can infer that this rock probably could contribute to increased concentrations of nitrogen in streams located in ombrophilus forest.

The presence of aluminum and iron in Latosols (Ultisols or Oxisols) could also explain the lower concentration of phosphate in all watersheds, since the former can cause the immobilization of this ion in soil. There is some evidence that phosphorus limits productivity in late-successional tropical forests (Vitousek et al. 1993). The concentration of inorganic phosphorus in streams, in general, were above the detection limits reflecting the low mobility of this ion. However, semi deciduous forests showed values ranging from 1 to 3 µM, which coincides with streams located in pasture in Rondônia, Brazil (Neill et al. 2001) with values ranging from 0 to 2.5 µM. In this same area, they found an N:P ratio > 80 to forested sites showing the P limitation in tropical ecosystems (Seitzinger 1988).

## CONCLUSION

Streams variations of major ions and inorganic nutrients composition could be associated to land use changes or soil characteristics. Streams located at Ribeira do Iguape (Streams 1, 2, 3 and 7) and Mogi Guaçu and Piracicaba watersheds (6, 9 e 10) presented the major differences in concentrations between undisturbed and disturbed areas with geomorphologic characteristics the main factor that drives the concentration in undisturbed areas, and urbanization and pasture in disturbed. Soil characteristics probably drives the $NO_3^-$, $Ca^{2+}$ and $Mg^{2+}$ concentrations in streams 1, 2 and 3 since that the ions in water, as soon as, in soils were higher at these watersheds. On the other hand, were not observed large differences between undisturbed and disturbed streams located at semideciduous forest. It could be observed that disturbed areas did showed an increase of ions concentration.

## ACKNOWLEDGMENTS

We wish to thank Instituto Virtual de Biodiversidade (BIOTA)-Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) Program for financial support (FAPESP project nº 01/03097-8). We are grateful to Fabiana Fracassi and Andréa Silva for lab assistance in the Laboratório de Ecologia Isotópica (CENA/USP). We also acknowledge personnel at Intervales, Morro do Diabo and Parque Estadual de Vassununga State Parks for assistance in field collections. We also wish to thank personnel at the UNH Water Resources Research Center for comments on draft manuscripts and we would like to thank Jim Hesson for the correction of this manuscript.

## RESUMO

A química da água é afetada por diversos processos que ocorrem no entorno da bacia de drenagem incluindo atividades antropogênicas que resultam em mudanças na qualidade da água bem como, no funcionamento desses ecossistemas. Portanto, o objetivo deste estudo foi avaliar a concentração dos íons dissolvidos ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $NH_4^+$, $NO_3^-$, $NO_2^-$, $Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$, $HCO_3^-$) em riachos no Estado de São Paulo (sudeste brasileiro). Os pontos de amostragem estão localizados em bacias não alteradas (floresta ombrófila densa, floresta estacional semidecidual e cerrado) e alteradas (pastagem, urbanização e cana de açúcar). A química dos riachos variou de acordo com o uso da terra, sendo as maiores concentrações encontradas, em geral, nas bacias alteradas. Riachos localizados em áreas pouco alteradas na Bacia de Ribeira do Iguape/Alto Paranapanema (riachos 1, 2 e 3) são, provavelmente, regulados pelas propriedades do solo desde que os riachos alterados (riacho 7) localizados na mesma bacia sob pastagem apresentaram maiores concentrações para a maioria dos parâmetros avaliados. Exceção aos riachos localizados na Bacia do Pontal do Paranapanema onde ambos os riachos, alterados (riacho 8) e pouco alterados (riachos 4 e 5), apresentaram padrões similares para a maioria das variáveis avaliadas.

**Palavras-chave**: hidroquímica, uso da terra, riachos, bacias de drenagem.

## REFERENCES

ANDRADE TMB, CAMARGO PC, SILVA DML, PICCOLO MC, VIEIRA SA, ALVES L, JOLY CA AND MARTINELLI LA. 2011. Dynamics of Dissolved Forms of Carbon and Inorganic Nitrogen in Small Watersheds of the Coastal Atlantic Forest in Southeast Brazil. Water, Air Soil Pollution 214: 393-408.

BALLESTER MV, MARTINELLI LA, KRUSCHE AV, VICTORIA RL, BERNARDES MC AND CAMARGO PB. 1999. Effects of increasing organic matter loading on the dissolved O-2, free dissolved CO2 and respiration rates in the Piracicaba River basin, southeast Brazil. Water Res 33: 2119.

BIGGS TW, DUNNE T AND MARTINELLI LA. 2004. Natural controls and human impacts on stream nutrient concentrations in a deforested region of the Brazilian Amazon basin. Biogeochemistry 68: 227-257.

BRUJINZEL LA. 1992. Nutrient input-output budgets of tropical forest ecosystems: a review. J Trop Ecol 7: 1-24.

BUTLER JN. 1991. Carbon dioxide equilibria and their applications. Chelsea, MI: Lewis Publishers, 260 p.

CAMPOS AEL, NUNES GS, OLIVEIRA JC AND TOSCANO IAS. 2009. Evaluation of contamination on Sabino streamlet (Basin Rio Tibiri) by heavy metals originated from waste and effluents of the Ribeira landfill, in São Luis island, state of Maranhão, Brazil. Quím Nova 32: 960-964.

CARACO NF AND COLE JJ. 1999. Human impact on nitrate export: An analysis using major world rivers. Ambio 28: 167-170.

CHRISTOPHER SF, PAGE BD, CAMPBELL JL AND MITCHELL MJ. 2006. Contrasting streams NO3 and Ca2 in two nearly adjacent catchment: the role of soil Ca and forest vegetation. Global Change Biol 12: 356-381.

CURRIE WS, ABER JD AND DRISCOLL CT. 1999. Leaching of nutrient cations from the forests floor: effects of nitrogen saturation in two long-term manipulations Can J For Res 29: 609-620.

DANIEL MHB, MONTEBELLO AA, BERNARDES MC, OMETTO JPHB, CAMARGO PB, KRUSCHE AV, BALLESTER MVR, VICTORIA RL AND MARTINELLI LA. 2002. Effects of urban sewage on dissolved oxygen, dissolved inorganic and organic carbon, and electrical conductivity of small streams along a gradient of urbanization in the Piracicaba River Basin. Water Air Soil Pollution 136: 189-206.

FAGANELLO CRF, FOLEGATTI MV, GONÇALVES RAB AND LUCAS FAT. 2007. Uso da água de irrigação e gestão de recursos hídricos na microbacia do Ribeirão dos Marins no município de Piracicaba/SP. Irriga 12: 456-470.

FENN ME, POTH MA, ABER JD, BARON JS, BORMANN BT, JOHNSON DW, LEMLY AD, MCNULTY G AND RYAN DF. 1998. Nitrogen excess in North American Ecosystems: predisposing factors, ecosystem responses and management strategies. Ecol Appl 8: 706-733.

GERMER S, NEILL C, VETTER T, CHAVES J, KRUSCHE AV AND ELSENBEER H. 2009. Implications of long-term land-use change for the hydrology and solute budgets of small catchments in Amazonia. J Hydrol 364: 349-363.

GUIMARÃES V AND SÍGOLO JB. 2008. Detecção de contaminantes em espécie bioindicadora (Corbicula fluminea) - Rio Ribeira de Iguape - SP/ Dectection of contaminants in a bioindicator species (Corbicula fluminea) - Ribeira de Iguape River, São Paulo State. Quím Nova 31: 1696-1698.

HOLLOWAY JM, DAHLGREN RA, HANSEN B AND CASEY WA. 1998. Contribution of bedrock nitrogen to high nitrate concentration in stream water. Nature 395: 785-788.

JORDAN C. 1985. Nutrient Cycling in tropical forests ecosystems. J Wiley & Sons, 200 p.

KAMISAKO M, SASE H, MATSUI T, SUZUKI H, TAKAHASHI A, OIDA T, NAKATA M, TOTSUKA T AND UEDA H. 2008. Seasonal and Annual Fluxes of Inorganic Constituents in a Small Catchment of a Japanese Cedar Forest near the Sea of Japan. Water Air Soil Pollut 195: 51-61.

LIKENS GE. 2004. Some perspectives on long term biogeochemical research from the Hubbarb Brook ecosystem study. Ecology 85: 2355-2362.

MARKEWITZ D, RESENDE JCF, PARRON L, BUSTAMANTE M, KLINK CA, FIGUEIREDO RO AND DAVIDSON EA. 2006. Dissolved rainfall inputs and streamwater outputs in an undisturbed watershed on highly weathered soils in the Brazilian cerrado. Hydrol Process 20: 2615-2639.

MARQUES PHC, OLIVEIRA HT AND MACHADO EC. 2003. Limnological study of Piraquara river (Upper Iguaçu Basin): spatiotemporal variation of physical and chemical variables and watershed zoning. Braz Arch Biol Technol 46: 383-394.

MARTINELLI LA, SILVA DML AND FERRAZ ESS (ORG). 2008. Cadernos de Bacias Hidrográficas do Estado de São Paulo, Piracicaba, 140 p.

MATSON PA, MCDOWELL WH, TOWNSEND AR AND VITOUSEK PM. 1999. The globalization of N deposition: ecosystem consequences in tropical environments. Biogeochemistry 146: 67-83.

MCDOWELL WH. 2001. Hurricanes, people and riparian zones: control on nutrient losses from forested Caribbean watersheds. For Ecol Manag 154: 443-451.

MCKEE LJ, EYRE BD, HOSSAIN S AND PEPPERELL PR. 2001. Impacts of climate, geology and humans on spatial and temporal variability in nutrient geochemistry in the subtropical Richmond River catchment. Mar Fresh Res 52: 235-248.

MIGUEL BO, ARMANDO SE, MIRIAM A, GIMENES ME AND NORA F. 2003. Monitoring organochlorine pesticides in surface and ground water in San Juan, Argentina. J Chem Chil Soc 48.

MULHOLLAND PJ. 1992. Regulation of nutrient concentration in a temperate Forest stream: roles of upland, riparian and instreams process. Limnol Ocean 37: 1512-1526.

NEILL C, DEEGAN L, CERRI CC AND THOMAZ S. 2001. Deforestation for pasture alter nitrogen and phosphorus in small Amazonian streams. Ecol Appl 11: 1817-1828.

NEILL C, DEEGAN L, THOMAS SM, HAUPERT C, KRUSCHE AV, BALLESTER MVR AND VICTORIA RL. 2006. Deforestation alters the hydraulic and biogeochemical characteristics of small lowland Amazonian streams. Hydrol Process 20: 2563-2580.

NIYOGI DK, SIMON KS AND TOWNSEND CR. 2004. Land use and stream ecosystem functioning: nutrient uptake in streams that contrast in agricultural development. Arch Hydrobiol160: 471-486.

OHRUI K AND MITCHELL MJ. 1998. Stream water chemistry in Japanese forested watersheds and its variability on a small regional scale. Water Res Resear 34: 1553-1561.

OMETTO JPHB, MARTINELLI LA, BALLESTER MVR, GESSNER A, KRUSCHE AV, VICTORIA RL AND WILLIAMS M. 2000. Effects of land use on water chemistry and macroinvertebrates in two streams of Piracicaba river basin, southeast Brazil. Fresh Biol 44: 327-337.

RAI SK, SINGH SK AND KRISHNASWAMI S. 2010. Chemical weathering in the plain and peninsular sub-basins of the Ganga: Impact on major ion chemistry and elemental fluxes. Geoch Cosm Acta 74: 2340-2355.

RAMIREZ A, JESUS-CRESPO A, MARTINO-CARDONA DM, MARTINEZ-RIVERA N AND BURGOS-CABARALLO S. 2009. Urban streams in Puerto Rico: what can we learn from the tropics? J North Amer Benthol Soc 28: 1070-1079.

SALOMÃO MSMB, COLE JJ, CLEMENTE CA, SILVA DML, CAMARGO PC, VITORIA RL AND MARTINELLI LA. 2008. CO2 and O2 dynamics in human-impacted watersheds in the state of São Paulo, Brazil. Biogeochemistry 88: 271-279.

SEITZINGER S. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance Limnol Oceano 33: 702-724.

SILVA DML, CAMARGO PB, LANÇAS FM, PINTO JSS, AVELAR WEP AND MARTINELLI LA. 2008. Organochlorine Pesticides in Piracicaba river basin (São Paulo/Brazil): A survey of sediment, bivalve and fish. Quím Nova 31: 214-219.

SILVA DML, OMETTO JPHB, LOBO GA, LIMA WP, SCARANELLO MA, MAZZI E AND ROCHA HR. 2007. Can land use changes alter carbon, nitrogen and major íon transport in subtropical Brazilian streams? Sci Agric 64: 317-324.

SILVA JSO, BUSTAMANTE MMC, MARKEWITZ D, KRUSCHE AV AND FERREIRA LG. 2011. Effects of land cover on chemical characteristics of streams in the Cerrado region of Brazil. Biogeochemistry 105: 75-88.

THOMAS SM, NEILL C, DEEGAN LA, KRUSCHE AV, BALLESTER MVR AND VICTORIA RL. 2004. Influences of land use and stream size on particulate and dissolved materials in a small Amazonian stream network. Biogeochemistry 68: 135-151.

TOMAZELLI AC, MARTINELLI LA, AVELAR WEP, CAMARGO PB, FOSTIER AH, FERRAZ ESB, KRUG FJ AND SANTOS Jr D. 2003. Dynamics of Dissolved Forms of Carbon and Inorganic Nitrogen in Small Watersheds of the Coastal Atlantic Forest in Southeast Brazil. Arch Biol Technol 46: 673.

VITOUSEK PM, WALKER LR, WHITAKER LD AND MATSON PA. 1993. Nutrient limitation to plant growth during primary succession in Hawaii Volcanoes National Park. Biogeochemistry 23: 197-215.

WANG XD, BURNS A, YANAI RD, BRIGGS RD AND GERMAIN RH. 2006. Changes in stream chemistry and nutrient export following a partial harvest in the Catskill Mountains, New York, USA For Ecol Manag 223: 103-112.