INPUT AND OUTPUT RATES OF SOME CHEMICAL SOLUTES IN SOROCABA RIVER

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Abstract: Considering the physical and chemical characteristics of the water of an aquatic ecosystem represent the result of the integration of many environmental factors, the aim of this study is presenting information about the rates of import and export of three inorganic nutrients in the Sorocaba River (part of the river that flows exactly within the Sorocaba city) and analyzing the effects of the land use and of the existence of effluents along the study area. After the sampling, the concentration of phosphate, nitrate and sulfate were determined in laboratory, by using the colorimetric method, for each one of the twenty four collected samples. Additionally, hydrological database was obtained from internet in order to estimate the import / export rates of the investigated compounds. The surveyed results indicate, respectively, rates of input and output of nitrite: 0.81 t x year⁻¹ and 64.24 t x y⁻¹ of phosphate 243.95 t x y⁻¹ and 130.10 t x y⁻¹ and sulfate 2,439.5 t x y⁻¹ and 6,098.8 t x y⁻¹. The study area also was considered eutrophic in the major part of the river, and hyper-eutrophic on four sampling points. So, it can be concluded that the studied water course, due to pass by a highly urbanized area and just after in a rural area, acts a source of nitrite and sulfate and as a sink of phosphate and it is strongly disturbed biogeochemically.

Keywords: Nutrients input and output. Environmental impact. Water resources. Sorocaba River. Water pollution.

1 Introduction

The physical and chemical characteristics of the waters of an aquatic ecosystem are the result of the integration of many environmental factors, some natural (chemical nature of the geological basement, relief morphology, soil and vegetation classes, climatic factors and morphology of the watershed, for example). There are others factors related with anthropogenic causes (number of inhabitant system of collecting and treating solid wastes and residual water, land cover patterns, level of agricultural mechanization and utilization of pesticides and fertilizers, among others) (SILVA et al., 2001; MARQUES et al., 2003; ESPÍNDOLA et al., 2004).

There is a large amount of chemical compounds in water bodies and the sources of these compounds are highly variable. A significant part of these compounds effectively participate in the metabolism of ecosystems (GUIRAUD et al., 2004). One example is the phosphate (PO₄³⁻), whose main natural sources are a) the weathering process of the geological basement (which results in the liberation of the elements) and b) precipitation of atmospheric particle materials (dry and wet). Important anthropogenic sources for the water bodies are the non-treated domestic and industrial sewage that is launched into the rivers (ESTEVES, 1998), along with the atmospheric particle material originating from industries.

Nitrite (NO₂⁻) is another compound that influences the metabolism of an ecosystem. This compound represents one of the two oxidized forms of nitrogen, constituting a more oxidized form. High concentrations are linked differently to the existence of organic pollution (ESTEVES, 1998; BRIGANTE & ESPÍNDOLA, 2003). There is also sulfate (SO₄²⁻), that occurs in significant fractions, together with hydrogen sulfide. The sulfate ion assumes greater importance in productivity of aquatic ecosystems since it constitutes the main form of sulfur available in the producers' community (ESTEVES, 1998).

Urban ecosystems represent areas where the human population lives in high density (> 186 inhabitants x km⁻²) and where there is a high number of people (commonly > 50,000 peoples), or where the urban infrastructure covers a significant portion of the Earth’s surface. Due to their peculiar dynamic of these ecosystems, they are sometimes the...
source of some compounds and other times the receptacle (KAYE et al., 2006).

In this context, the Sorocaba River, together with the city of the same name, is a classic case of intense environmental alteration, mainly due to the intensive urbanization process that has been occurring in the city. This has made the drainage area of the Sorocaba River more and more impermeable, but the environmental consequences of this alteration have been poorly studied up to now. Among the studies already carried out, Ribeiro et al. (1995), Fagundes (1997), Smith & Barrella (2000) and more recently Silva et al. (2006) can be cited. These studies had different aims and investigated different parts of the Sorocaba River.

Considering this, the aim of this study was to estimate the input and output rates of phosphate, nitrite and sulfate on the Sorocaba River (the part that encompasses Sorocaba city) and to analyze the effects of land use and the effects of the existence of sewage launched into the analyzed segment of the river.

2 The study site

Sorocaba city is located in São Paulo State, between coordinates 23º 21' and 23º 35' South Latitude and 47º 17' and 47º 36' West Longitude. It encompasses an area of 449 km² and contains a population of 552 inhabitants (98% considered urban). On the other hand, the Sorocaba River is the principal water course that passes by the city and crosses urban and rural lands (Figures 1 and 2).

The climate is classified as “Cfa” (hot subtropical) according to Köeppen’s classification system. The annual average temperature is 21.4°C, presenting a maximum of 30.1°C and minimum of 12.2°C. The annual rainfall depth is 1,285 mm (SILVA, 2004).

According to Paula et al. (2006), the surface relief of Sorocaba city is predominantly flat, although concave and convex slopes also occur widely throughout the region. The main soil classes are: Alfisols and Oxisols, although Inceptisols and Entisols are also found (OLIVEIRA et al., 1999).

3 Procedures (sampling and analyses)

The Sorocaba River is approximately 180 km in length (considering the natural sinuosity of the river), from its principal headwaters until it joins with the Tietê River (RIBEIRO et al., 1995). Twenty three sampling points were established in the part of the Sorocaba River that enters Sorocaba city, jointly with one located in Votorantim city (approximately 2000 meters upstream from the first sampling point located within the Sorocaba city, Figure 3). The sampling point located in Votorantim was important for verifying the chemical and physical situation of the water before the water of the river entered into the study area (Sorocaba city). The average distance between each sampling point was 2000 meters, even when considering the sinuosity of the drainage channel of the Sorocaba River. The sampling activities were performed on February 14th and 15th, 2006, using an appropriate collector. The climatic conditions on these days were adequate since neither of them was preceded by rain.
Figure 2 – Land cover map of Sorocaba city. Source: Silva (2004).

Figure 3 – Waterway and spatial presentation of the sampling points.
Investigative parameters

For each sampling point, one sample of approximately 2.0 liters was collected. In laboratory, the concentrations of phosphate, nitrite and sulfate were determined by colorimetric method using a Hach DR/2000 Spectrophotometer.

Estimative of charge of nitrogen and phosphorus and determination of the Trophic State Index

The biogeochemical traces of phosphate, nitrite and sulfate were estimated by analyzing the concentrations of the compounds from the twenty four sampled points and also the flow of the Sorocaba River on the part considered. The database used for flow (period: 1978 – 2003) was acquired at the website of the São Paulo Department of Water and Electric Energy (DEPARTAMENTO DE ÁGUAS E ENERGIA ELETRICA, 2006). The obtained flow data is concerning to the DAEE’s 4E-018 fluviometric station, located at Raposo Tavares highway, near point number two of this study. On the other hand, the flow values, after conversion from m$^3$ x s$^{-1}$ to liters x year$^{-1}$, were multiplied by the concentration of each compound, in order to estimate the values of flux in “tons x year$^{-1}$”, according to Henry & Gouveia (1993).

Additionally, in order to establish a comparative analysis of the regional hydrology a pluviometric database (monthly average values) was acquired from the climatologic station located in Sorocaba city. Both the fluviometric and pluviometric database correspond to the same period.

The charge of nutrients was also estimated. Such information was surveyed according to methodology proposed by Arceivala and described with details in Prado et al. (2003) for nitrogen and phosphorus. The equations used were:

Annual weight of phosphorus:

$$P = H \times \alpha \times 0.002 \times 1000 \times 1$$

Annual weight of nitrogen:

$$N = H \times \alpha \times 0.008 \times 1000$$

Where,

- $P$ = annual weight of phosphorus for a determined year, in tons.
- $N$ = annual weight of nitrogen for a determined year, in tons.
- $H$ = number of inhabitants for the year “a”.
- $\alpha$ = number of the days in a year (= 365).

Numbers were computed for three periods (1988, 1995 and 2004). This determination was useful in helping us comprehend the amount of phosphorus and nitrogen according to increases in population. The database regarding the population of Sorocaba city for the years investigated was acquired from the Foundation for Data Analysis of São Paulo State (2006).

The Trophic State Index (TSI) was determined according to the manner proposed by Carlson (PRADO et al., 2003; COMPANHIA ESTADUAL DE TECNOLOGIA EM SANEAMENTO AMBIENTAL, 2006). For this method, which is formed by a mathematical expression, the phosphate concentration value ($PO_4^{+}$) is required, giving the equation:

$$TSI \ (PO_4^{+}) = 10 \times \left\{ 6 - \left[ \ln \left( \frac{21.67}{PO_4^{+}} \right) / \ln 2 \right] \right\}$$

According to the resulting value, the water body (lake or river) is considered oligotrophic when TSI $\leq$ 44, mesotrophic when 44 < TSI $\leq$ 54, eutrophic when TSI 54 < TSI $\leq$ 74 and hypereutrophic when TSI $\geq$ 74 (BRIGANTE & ESPÍNDOLA, 2003).

This is common when evaluating the TSI by means of an integrated computation, also using data on total phosphorus, water transparency and chlorophyll. Due the fact that we only had data about phosphate, the TSI was determined exclusively through this parameter (phosphate). However, we consider that the TSI determined exclusively with phosphate concentration is sufficiently representative for an accurate determination of the TSI of the local studied.

4 Results and discussion

Figure 4 shows the pluviometric and fluviometric data (average) for each month. It can be observed that the lowest observed value for flow was 11.8 m$^3$ x s$^{-1}$ for July and the highest value was 14.6 m$^3$ x s$^{-1}$ for February. The seasonal variation of the river flow database was considered low expressive. This can be explained by the regularized flow of the Sorocaba River due to the location of the...
Itupararanga Dam a few kilometers upstream from Sorocaba city. However, during all months, the values of the last five years of the database were below the average value. Additionally, although there is a regularized flow, Sorocaba city has undergone flooding in the central area of the city in practically all years (normally from December to March). The annual average value estimated for flow of the Sorocaba River was 12.9 m$^3$ x s$^{-1}$.

On the other hand, the pluviometric data showed that the driest month is August, presenting an average value of 29.4 mm x month$^{-1}$. The rainiest month was January, with 253.7 mm x month$^{-1}$ and the annual rainfall depth was 1,307.5 mm. The correlation analysis computed between the pluviometric and fluviometric database resulted in $r^2 = 0.79$ (significant $\alpha=1\%$).

This data is important for understanding the seasonal dynamic of the nutrients in Sorocaba city and also in the Sorocaba River proper as a major input of nutrients is predicted in the rainy periods, a consequence of the diffuse pollution from high runoff rates resulting from heavy rains.

Regarding nitrite, it was verified that from point 1 to point 7 (Figure 5) concentrations were significantly low, showing a considerable increase from point 8 and with high variation along the studied part of the river. The highest observed value was 0.64 mg x L$^{-1}$ and the average value was 0.24 mg x L$^{-1}$.

Similar to this study, Brigante & Espíndola (2003) also registered a significant increase in the nitrite concentrations for the Mogi-Guaçu. The tendency towards increasing occurred from headwater region to estuary region, although the sampling points themselves were located, more distant than the points of this study. These authors affirm that nitrite is a good indicator of organic pollution for rivers and reservoirs and such information can be seconded here as the values for nitrite effectively increased after the passage of the water through the urban area and greater demographic concentration of Sorocaba city.

![Figure 4 - Average values of monthly fluviometric (m$^3$ x s$^{-1}$) and pluviometric (mm x month$^{-1}$) database. Source of the databases: DEPARTAMENTO DE ÁGUAS E ENERGIA ELÉTRICA (2006).](image)

After computation of nitrite concentration at the first and last sampling points of the studied area, it was estimated that, via the Sorocaba River, there was an input of nitrite of 0.81 tons x year$^{-1}$ and an output of 64.24 tons x year$^{-1}$. Thus it can be concluded that the nitrite estimate was surely positive. This indicates that Sorocaba city can be considered a source of nitrite for the Sorocaba River.

The evolution of phosphate concentrations along the studied part of the Sorocaba River is shown in Figure 6. It can be observed that peak concentration occurred at point 8, which was six times higher than the average value (average value: 0.5 mg x L$^{-1}$). On the other hand, the lowest value was found at point 3 (0.2 mg x L$^{-1}$). It is difficult to establish the exact cause of this abrupt increase, which occurred (so markedly) only for this sampling point exactly on this region of
the river because after this peak there was an abrupt decrease in the values obtained at subsequent sampling points. It is important stating that the laboratorial procedures for this sampling point (point 8) were performed repeatedly three times in order to reject the supposition of laboratory mistakes. The results of these repetitions were very similar among themselves. After the occurrence of such a high (and specific) concentration of phosphate, subsequent sampling points continued presenting low variation in concentration, showing a new increase at point 19, followed by new decreasing in subsequent sampling points.

![Figure 5 - Evolution of nitrite concentrations along the studied segment of the Sorocaba River.](image)

The computed estimate established for the phosphate indicated that the imported amount of this compound via Sorocaba River was 243.95 tons x year\(^{-1}\) and the exported amount was 130.10 tons x year\(^{-1}\). This data indicates that the study area can be considered a receiving area for the phosphate as the resulting value between exportation – importation was negative (-113.85 tons x year\(^{-1}\)). This is an acceptable inference since phosphorus is considered a scarce element and ecosystems normally have a tendency to absorb phosphorus, or this element tends to be deposited, according to aerobic or anaerobic conditions of the body of water (ESTEVES, 1998).

Values of phosphorus higher than 0.3 mg x L\(^{-1}\) stimulate the proliferation of algae, favoring the eutrophication process (BRANCO, 1986 in BRIGANTE & ESPÍNDOLA, 2003). Though this study did not quantify the phytoplanktonic community of the Sorocaba River, it can be deduced that this environment effectively has a high capacity of primary production by phytoplankton. On the other hand, the occurrence of macrophytes like Eichhornia sp was observed in situ in some parts of the river, especially in those parts whose flow velocity was low and, in some cases, with a connection to marginal lagoons. There was also occasional occurrence of grass Brachiaria sp. along the margins of the river. This might be an indicator of the eutrophication process that the Sorocaba River has been experiencing, as also verified Espíndola et al. (2004) for the Salto Grande reservoir (Americana – SP). Smith & Barrella (2000) found a major concentration of clusters of other species of macrophytes, such as Salvinia sp., Elodea sp. and Nymphaea sp., mainly in marginal lagoons located in some parts of the Sorocaba River (species not observed on this study).

Sulfate presented values that changed from 6 mg x L\(^{-1}\) (point 1) to 17 mg x L\(^{-1}\) (points 13 and 15, Figure 7), with an average value of 12.5 mg x L\(^{-1}\). A significant increase in the values of sulfate was found between sampling points 11 and 12, which continued up to the last sampling point investigated.
The main forms of input of sulfate in aquatic ecosystems are: pluviometric precipitation, rock weathering and agricultural activities (ESTEVES, 1998). In fact, an abrupt increase between sampling points 10 and 11 was observed. Such sampling points are located in a part where land use changed from urban to rural, also occurring in places with poorly managed pig breeding, where manure is thrown directly into the river. On the other hand, patches of riparian vegetation presenting excellent states of conservation were noted; the topography of the region where riparian vegetation occurred was flat, disfavoring runoff.

Additionally, an odor that typically occurs in anaerobic environments was also noted in these rural regions where the topography is predominantly flat. This fact was also observed by Espíndola et al. (2004) for the Salto Grande Reservoir. These authors interpreted such odor as deriving from the advanced eutrophication process that this reservoir has experienced. For this complex dynamic, it is difficult to establish an exact understanding about the biogeochemistry of sulfate in the Sorocaba River. Hence, complementary and detailed studies are strongly needed in order to delineate concrete conclusions concerning this process.

Considering both the computed value of river flow together with the sulfate concentrations of sampling points 1 and 24, it was estimated that the region has been receiving approximately 2,439.5 tons x year\(^{-1}\) via the Sorocaba River, with outputs of approximately 6,098.8 tons x year\(^{-1}\). Thus it is verified that a gain of 3,659.3 tons x year\(^{-1}\) occurs on the studied segment of the Sorocaba River and that the drainage area of the Sorocaba River located within the municipal boundaries of Sorocaba constitutes a significant source of sulfate for this lotic system.
The relationship between the presence of sulfur compounds in the system and the dynamic ecosystem is complex. Normally, there is a relationship with the oxygen dynamic since in the absence of oxygen sulfur is the element used as an electron acceptor in the metabolic processes of aquatic ecosystems (ESTEVES, 1998). For this study, the relationship between values of sulfate and dissolved oxygen (data concerning dissolved oxygen were acquired at the same sampling points and dates and yet are not published), resulted in a correlation value of $R^2 = -0.89$ (significant $\alpha = 1\%$).

In regard to the estimate of nitrogen and phosphorus present in Sorocaba city, Martinelli et al. (2002) and Prado et al. (2003) point out that population increase is one of the main causes of the degradation of the water quality of water resources because increased sewage occurs in direct proportion to population increase and this sewage is commonly launched into water bodies. For this study, it was verified that from 1985 to 2004, the amounts of nitrogen and phosphorus increased 76% for Sorocaba city, as verified in Table 1.

### Table 1 – Amounts of nitrogen and phosphorus produced in the study area (tons x year$^{-1}$) for 1985, 1995 and 2004.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1985</th>
<th>1995</th>
<th>2004</th>
</tr>
</thead>
<tbody>
<tr>
<td>Population</td>
<td>314,101</td>
<td>427,336</td>
<td>552,194</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>917.2</td>
<td>1,247.8</td>
<td>1,612.4</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>229.3</td>
<td>311.9</td>
<td>403.1</td>
</tr>
</tbody>
</table>

Studying the dumping of sewage into several rivers in Sào Paulo State, Martinelli et al. (2002) verified that only 30 cities (out of a total of 645) are responsible for 78% of the total amount of domestic sewage produced throughout the entire state. As these cities treat only a small amount of such sewage, the remaining amount is highly concentrated in these cities. This is the case in Sorocaba, which was classified by these authors as one of the 30 most polluted cities in Sào Paulo State.

In Sorocaba city, the volume of sewage that has been treated is still far from the ideal volume and logically this brings with it many local and regional biogeochemical disturbances (such as those we are reporting) and many microbiological consequences, too, as reported by Ribeiro et al. (1995). These authors verified a significant degradation of the water quality of the Sorocaba River in microbiological terms after the water passes by the urban area of Sorocaba city. They noticed a significant increase of bacteria colonies of anthropogenic / sanitation and also of hospital origins, showing the great influence that human occupation has exerted on the water quality of the rivers in terms of this aspect.

The Trophic Index State for the studied segment of the Sorocaba River, computed by using equation (3) and presented in Figure 8, showed that along the part studied the river presents predominantly eutrophic characteristics, and presents hyper-eutrophic characteristics at four sampling points. The values ranged from 58.8 to 99.9 (dimensionless). This confirms the current and actual situation of the Sorocaba River concerning the grave pollution that the river has suffered.

This classification is specific for this sampling period (February 14 and 15, 2006). On the one hand, it is well established that there is a seasonal variation of the STI for a same place, as pointed out by Brigante & Espindola (2003) for Mogi-Guacu River and also pointed out by Prado et al. (2003) for the Piracicaba and Tietê Rivers (near Barra Bonita Reservoir). On the other hand, the STI registered for this study for many parts of the Sorocaba River probably tends become more aggravated in other periods of the year because the sampling of this study was performed during the rainy season (when the flow of the Sorocaba River was high). For this season, it is highly possible that the pollutant substances were more dissolved than in the period when the river presents less flow. In the dry season, the concentration of pollutants, particularly phosphate and other elements responsible for the eutrophication process, might be significantly higher.

Another fact registered during the sampling activities was the presence of solid
wastes on the surface of the river (pieces of plastic - PET bottles - were the most common), in quantities that represented tons x day\(^{-1}\). Hence the necessity of programs related to the environmental education of the population and the clean-up of all urban drainage system can be verified, including cleaning and maintaining of pluvial water collectors and drainage.

5 Conclusions

According to the information surveyed here, it can be concluded that the part of the Sorocaba River studied has acted as a source of some elements, as in the case of nitrite and sulfate compounds, and a receiving are for others, such as phosphate compounds.

The STI computed here allows us to infer that the ecological situation (especially in regard to pollution) of the Sorocaba River is grave, and the tendency is towards ever more degradation if the population continues to increase, with consequent increases in the amount of nitrogen and phosphorus dumped into the river.

The current situation of the Sorocaba River requires urgent actions aimed at minimizing the input of pollutants and others aimed at regulating land use, mainly of riparian zones, both in urban and in rural areas.

6 Taxas de entrada e saída de alguns compostos químicos no Rio Sorocaba

Resumo: Considerando que as características físicas e químicas das águas de um ecossistema aquático representam o resultado da integração de vários fatores ambientais, o objetivo deste trabalho é apresentar resultados sobre as taxas de importação e exportação de nutrientes inorgânicos no rio Sorocaba (trecho que compreende o município de Sorocaba), e analisar os efeitos do uso do solo e da existência de efluentes ao longo do trecho analisado. Após coletas das amostras de água, determinaram-se por colorimetria as concentrações de fosfato, nitrito e sulfato. Os resultados indicaram taxas de importação e exportação, respectivamente, de nitrito: 0,81 t x ano\(^{-1}\) e 64,24 t x ano\(^{-1}\); de fosfato 243,95 t x ano\(^{-1}\) e 130,10 t x ano\(^{-1}\) e de sulfato 2.439,5 t x ano\(^{-1}\) e 6.098,8 t x ano\(^{-1}\). O trecho investigado foi ainda considerado eutrófico em sua maior parte e hipereutrófico em quatro pontos. Desta forma conclui-se que o trecho do rio estudado, em função de passar por uma área altamente urbanizada e logo em seguida rural, atua como uma fonte de nitrito e sulfato e como um sumidouro de fosfato, estando profundamente desbalanceado biogeocquivamente.

7 References


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