ANTHROPOGENIC FACTORS DRIVING PHOSPHORUS CONTENTS IN SALTO GRANDE RESERVOIR SEDIMENTS, SÃO PAULO STATE (SE BRAZIL)

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Abstract

Phosphorus is an essential element for life and, when scarce, this macronutrient is a limiting factor for primary production. Phosphorus (P) is a widely used element in the composition of fertilizers, besides being present in large quantities in domestic effluents. Its accumulation in the springs is related to the proliferation of algae and cyanobacteria. In excess, P is a pollutant that contributes greatly to the eutrophication, development of reduced conditions and deterioration of water bodies. In order to understand how the anthropogenic action affected the accumulation of P in the freshwater reservoir of Salto Grande, Americana City (São Paulo State, Brazil), the evaluation of a temporal sedimentary record was carried out. For this purpose, a sediment core collected in the reservoir of Salto Grande was studied. The sediment core recorded the reservoir history since its filling in 1950. The comparison of P concentrations along the core with the population growth curve indicates that the population growth in the surrounding region has had a direct impact on the accumulation of P in the freshwater reservoir of Salto Grande. The eutrophication history of this major continental ecosystem of São Paulo State, was reflected by this sewage-derived from loading of P.

Keywords: Phosphorus. Chemical Markers. Eutrophication. Environmental. Impact. Freshwater Reservoir.

1. Introduction

Aquatic systems are recognized as being integrators of natural and anthropogenic processes; as final sinks of contaminants, these systems become excellent markers of anthropogenic interference and environmental impacts (Esteves, 2011).

Sediments can be considered pollutant sinks, with clays having the highest adsorption capacity; however, pollutants can return to the water column and be available to the biota if there is bioturbation, changes in hydrodynamics and physicochemical conditions (pH, dissolved O2, conductivity, reduction potential) of the environment (Espindola et al., 2004). In this way, reservoir sediments act as deposits of allochthonous and autochthonous material, acting as a true database of the water bodies (Esteves, 2011). This database can be accessed from data recorded in sediment cores, allowing to preform paleoenvironmental reconstructions and evolutionary models of the sedimentary environments along the geological time (Förstner, 1976; Bryan and Langton, 1992; Misailidis et al., 2017).

In view of the above considerations, the present work evaluates the use of phosphorus as a natural element and product of anthropic activity that is a chemical marker of the intensity of anthropic interference in the environment.
1.1 Phosphorus

A great attention has been given to phosphorus (P) because it is an essential element, involved in main biological processes, participating as a component of the cell membrane (phospholipid), genetic material (ribonucleic acids DNA and RNA), phosphoproteins (casein and vitelline), enzymes and vitamins (Nelson and Cox, 2011). It is important to emphasize its importance as a limiting factor in the productivity of aquatic environments, regulating the primary productivity of the ecosystems along with nitrogen (N) (another important macronutrient), keeping a ratio of 1P:16N for algae (Wetzel, 2001). However, high concentrations of P give rise to processes of eutrophication of water bodies, making the evaluation of their concentrations a proxy for monitoring the degree of eutrophication of water bodies (Schindler et al., 2008).

Phosphorus is found in aquatic environments in several physical states (Stumm and Morgan, 1995), such as: i) PH$_3$ gas, phosphine (IUPAC name: phosphane), found in sediments mainly from anoxic environments (Wetzel, 2001); ii) dissolved inorganic phosphorus (DIP) (Orthophosphate, hydrogen phosphate and phosphoric acid respectively PO$_4^{3-}$, HPO$_4^{2-}$, H$_2$PO$_4^-$), being the P-ortho form the most assimilated by bacteria, microalgae, algae and macrophytes and the last two species most prevalent in fresh water; iii) dissolved organic phosphorus (DOP), such as colloids, phosphate esters and nucleotides that are produced by living or decomposing organisms; iv) particulate OP that is represented by excretions produced by living organisms or debris from dead organism in sediments; v) particulate IP (PIP), represented by species of P (P(OH)$_3$) adsorbed to particulate material such as silt and clay particles.

The main sources of phosphorus in the aquatic ecosystems are the natural ones, coming from the weathering of the rocks that constitute the drainage basin, mainly constituted by apatite Ca$_5$(PO$_4$)$_3$(OH, F, Cl), from the leaching of surrounding soils and atmospheric spray. In continental ecosystems, the main sources other than natural ones originate from anthropic activities mainly through industrial and domestic effluents (Newman, 1995; Smil, 2000; Wetzel, 2001).

1.2. The main goals

The main aim of this work is to evaluate the behavior of the phosphorus and its permanence in the sediments of the freshwater reservoir of Salto Grande, Americana, São Paulo State, Brazil. It is also intended to analyze the relationship between the temporal evolutions of the sedimentary concentrations of phosphorus with the activities around the reservoir and to evaluate the intensity of the anthropic interference.

2. Geological setting of the study area

The Salto Grande Reservoir (SGR) is located in the municipality of Americana-SP (coordinates 22º44' S and 47º19' W) and is part of the Atibaia River basin (Fig. 1). It is located in the São Paulo peripheral depression in the middle Tietê area and is part of the Piracicaba, Capivari and Jundiaí river basin, formed by the damming of the Atibaia River.

![Sampling point (red star) in the Reservoir of Salto Grande (reproduced from Misailidis et al., 2017).](image-url)
The Atibaia River, the main tributary of the reservoir, is formed from the confluence of the Atibainha and Cachoeira rivers, both sources of the Greater São Paulo Metropolitan Region and are the main constituents of the Cantareira System. The Atibaia River runs a length of 154 km until its impoundment, attending 20 municipalities.

The SGR receives effluents from the Paulínia Petrochemical Complex and Campinas city, in addition to the other cities present along the course of the Atibaia River. The expressiveness of the occurrence of Latosol and Clay soil reflects the geological and geomorphologic context in which the reservoir is inserted (Fonseca and Matias; 2014).

The SGR is located in a geologically stable environment, located on the eastern edge of the Paraná Basin peripheral depression, characterized by an area with a smooth topography formed by a hilly terrain with rectilinear slopes of low angle, which favors a slower surface flow; occurs on a silo (intrusive rock in the form of a sill) of the basalt of the Serra Geral Formation, which is sandwiched with the sandstone units of the Itararé Group (IPT, 1981).

The occurrence of basic igneous rock and the smooth topography, which guarantees a slower runoff of rainwater, added to the geological stability of the region, favor the development of Latosols and Argisols, these categories of soil are very common in the region of the peripheral border of Paraná Basin (IPT, 1981).

2.1 Climate Characteristics

According to the Köppen-Geiger classification, the climate in the study area transits between the humid temperate climate with dry winter and the hot and humid summer (Cwa) (Peel et al., 2007). The annual mean precipitation in the reservoir region is in average of 1300 mm, according to the historical measurement series, between 1937 and 2014, made available by the Agência Nacional da Água (National Water Agency) (ANA, 2016) (Fig. 2).

The rainfall in the study area is characterized by the interaction of tropical systems, with the South American summer monsoon, operating between October and May (Rao et al., 1996). Between the late autumn and winter, precipitation is associated with the entry of cold fronts generated by the influence of the polar air masses of the South Atlantic. During the summer, precipitation is associated with the convective activity of the South Atlantic Convergence Zone (Vera et al., 2006; Marengo et al., 2012).

The SACZ is characterized by a transient convective system formed by the displacement, via low level jets, of the surplus moisture from the western region of the Amazon to the southeast of Brazil, constituting a band of NW-SE direction cloudiness that extends until the South Atlantic subtropical ocean. For this reason, most of the rain that falls on the region is related to the South American monsoon system (Vera et al., 2006; Marengo et al., 2012).

The seasonality of the regional precipitation regime can be observed in Figure 3, which shows the behavior of the monthly precipitation averages measured in the 1937-2014 series (ANA, 2016). In the rainy season, practically 90% of the average annual accumulation is concentrated between October and March, while during the dry season, between April and August, the average quarterly accumulation amounts to around 100 mm, nearly only 8% of the yearly accumulated precipitation (ANA, 2016). The reduction of the reservoir flow, during the dry season, results in an increase of...
the water residence time, with consequent interference in the aquatic biota of the reservoir (Tucci et al., 2004).

The average annual temperature ranges from 18.2 to 24.9 °C, with a maximum of 35 °C in the rainy season (summer) that occurs between October and March, and a minimum of 4.4 °C in the dry season (winter April to September (Peel et al., 2007). Seasonal variations of local temperature influence evapotranspiration rates, storage, deficiency and water surplus in the reservoir (ANA, 2016).

2.2 Characteristics of the surrounding area

The area of the reservoir is longitudinally divided, being the north flank, the zone with the greatest predominance of agricultural activity and main occurrences of areas of natural vegetation. On the left side of the dam, urban occupation with anthropized areas (construction, orchards, landscaping), populous neighborhoods (Praia Azul and Praia dos Namorados), farms, sites and condominiums (Fig. 4) represent the current land uses around the SGR. The flow of surface water from the environment, as well as the mainly domestic emission of effluents, provide an increase in nutrient concentration, favoring flowering and biomass production (Lopes et al., 2014). As a result, the nutrients and biomass increment contribute to the increase of sedimentation of the reservoir, which benefits macrophyte species (Tavares et al., 2004).

3. Material and methods

This work analyzes the results obtained in a sediment core collected in the SGR (22°43'29.4"S and 47°13'51.3"W). The site where the core was collected (Fig. 1) is located about 1300 m from the west bank and 900 m from the east bank, with a water column depth of 14 m.

The sediment core was collected during the dry season (May 27, 2015), by means of a witness to gravity, following the sampling technique of Subgeo - Commerce of Nautical Equipment and Submarine Technical Services.

In this technique, the crimping of the sampler is performed from the percussion of a weight which is thrown against a transverse rod attached to the sampler tube. The progressive elevation of this weight as well as the removal of the core was controlled by divers.

The core transport was carried out with extreme care to avoid contamination of the lower layers with chemical elements of the upper layers.

The core was taken to the laboratory of the Oceanographic Institute, of the São Paulo University (IO-USP), where it was opened and sliced; the first centimeters (8-16 cm) were sampled, in a single slice of 8 cm due to the fluidity of the sediments, after 16th cm the samples were sectioned every 4 cm until the 24th cm, and in sequence, after this interval towards the base they were sectioned every 2 cm. The slices were placed in plastic vials and taken to the refrigerator (4°C) until freeze-dried. Before storing the sediments, the vials were flushed with "extran" (MERK) and with deionized water, then submerged in 10% HNO₃ solution for 24 hours with subsequent drying in order to remove any contaminant from the vials.

Granulometric analyzes were performed at the Sedimentology Laboratory of the Institute of Geosciences, of São Paulo University (IGC-USP). These analyses were performed with a laser-diffraction grain size meter (Malvern Mastersizer 2000 equipment). The textural parameters were
analyzed according to Folk and Ward (1957). The sediments were macerated and homogenized, and then the organic material and carbonates were removed by hydrogen peroxide attack. The sample was oven dried and homogenized. An aliquot of 2 grams of the dry sediment was placed in a liter of water with a dispersant (sodium pyrophosphate), keeping the system under ultrasound to disaggregate the sample. The data obtained by Malvern Mastersizer were converted into percentages of different size fractions.

The phosphorus determinations, subdivided in the inorganic phosphorus (IP), organic phosphorus (OP) fractions were carried out at the Biogeochemical Laboratory of the Geochemistry Department of the Universidade Federal Fluminense.

The extractions of IP and total phosphorous (TP) fractions were performed according to the method proposed by Aspila et al. (1976) and its concentrations were obtained by the colorimetric method proposed by Grasshoff et al. (1983). Phosphorous reacts with acidified molybdate, producing a phosphomolybdate complex, later reduced by ascorbic acid to a blue compound. The concentration of OP was calculated from the difference between TP and IP fractions.

In order to evaluate the anthropic intervention in the SGR system, the obtained data of phosphorus concentrations in the several fractions were plotted together with the data of population growth, obtained from reports published by IBGE (2010) and precipitation curves.

4. Results and Discussion

4.1 Grain size analysis

The grain size analysis allowed to describe the changes of depositional environment after the filling of the reservoir. As shown in Figure 5, the most relevant changes are observed in the percentage of sand and clay.

While in the “Pre-Reservoir Phase”, before filling, it is seen a larger percentage of sand grains with 9.1% in the average and clay presents a lower percentage with 18.9% and silt with 71%, at the “Reservoir Phase” there is an increase in clay percentage to 26.4% and sand has a significant decrease in its percentage falling to 2.2%, while silt maintains the average of proportionality with a tendency to increase towards the top.
4.2 Sedimentary facies

The sedimentary facies of the Pre-reservoir Phase, recorded between 232 cm and 160 cm, is identified by a clear sedimentary discontinuity marked by a sudden and slightly irregular contact, as can be seen in Figure 6.

The transition in the sedimentary sequence of the “Pre-Reservoir Phase” for the “Reservoir Phase” is marked by a clear change in the particle size, with a substantial increase in the proportion of clay (16–30%), followed by a decrease in the concentration of coarse and medium silt fractions (46–36%), as shown in Figure 5. This unit still has a large amount of plant remains, such as fiber and plant roots. Between 210 cm towards the base of the sediment core there is a gradual transition to clayed, pale grayish levels with a variegated texture formed by spots of ocher color, which grades to a mottled pattern closer to the base. This sedimentary sequence is attributed to the units of soils and sediments deposited in the alluvial plain of the Atibaia River.

The sedimentary sequence of the “Reservoir Phase” can further be divided into two subunits: “Reservoir Phase I” and “Reservoir Phase II”. Reservoir Phase I: between 162 cm and ~140 cm, is marked by massive sedimentary facies, where it is not possible to clearly recognize stratification. This subunit shows light brown sediments with predominance of silt sediments (~68%) and clay (~29.5%). Reservoir Phase II: is marked by plane parallel stratification, formed by centimetric layers (1-2 cm) of black-colored mud interspersed with layers of light brown mud, similar to that of Reservoir Phase II.

The fluidity of the sediment can be seen in the deformation of the stratification at the top of Reservoir Phase II (Fig. 6). Like the sediments from the previous phases, a silt particle size fraction (~71%) followed by clay (~26%) predominated. The rhythmicity of the succession of light and dark layers is characteristic of the sequence between 177-34 cm and can be attributed to interannual variations of the deposition rate of organic matter associated to the seasonal variations of productivity in the reservoir. In all, about 40 pairs of layers were counted, indicating that this sequence is at least 40 years old, since annual seasonal precipitation is expected to be recorded as pair of bands, as clear and dark layer.

4.3 Phosphorus (P) variability

The Figure 7 shows the evolution curve of the TP, OP and IP fractions of the sediments. As it is possible to observe the concentrations of TP present a clear increase towards the top. Along the sedimentary profile, there is an expressive increase in the concentration near 95 cm depth, characterized by a jump in TP concentrations.

The contributions of IP are the most representative, adding up to ≈84 % of the total P found in the sediments.
The values of TP measured at the core top (~1200 μg/g) are comparatively slightly higher than the results obtained in previous studies that indicate values in the order of 858 μg/g (Leite, 2002).

In general, the concentrations of TP measured in the GSR sediments present moderate values, on average 1200 μg/g. As a reference, we can cite the values recorded in sediments of other reservoirs, such as the values measured in the sediments of Billings Reservoir (one of the largest and most important water reservoirs in the Metropolitan Region of São Paulo) of 5000 μg/g (Mozeto et al., 2003) and 5316 μg/g in Lago das Garças (Jesus, 2008), also located in the metropolitan region of São Paulo.

Fig. 7. Total phosphorus (TP), inorganic phosphorus (IP) and organic phosphorus (OP) concentrations curves. The red dashed line indicates the depth in which the change of depositional environment is recorded.

The concentration values of TP, IP and OP obtained in the main core phases are summarized in Table 1, evidencing that temporal changes are dominated by IP variability.

By means of the phosphorus evaluations, there is a tendency of increase in the concentrations of TP, from depths between 177 cm and 160 cm (intersection between the soil phase and the period of flood of Salto Grande Reservoir) towards the top, with IP being its major contributor. OP, on the other hand, presented concentrations with regular variations throughout the core length (Fig.7), suggesting a probable continuous influx of nutrients into the system.

This interpretation is plausible, since there was always some anthropic influence around the reservoir, whether related to agricultural activities (with the use of organophosphate and organochlorine fertilizers and pesticides) and/or specific provisions of domestic and industrial sewage from the chemical industries that were installed since the 70’s.

The presence of IP in the water column occurs mainly in the forms of the orthophosphate ion (PO₄³⁻) and in lower concentrations in the form of HPO₄²⁻ and H₂PO₄⁻ (Esteves, 2011). Domestic effluents, especially detergents, usually account for more than half of the total P contribution in anthropogenic systems (Esteves, 2011).

Due to the contribution of domestic effluents in the concentration of IP to the water column and, consequently, to sediments, a comparison of the IP curve with the population growth rate of the region of Americana city is shown in Figure 8. For the comparison, we assumed the year of 1950 as the beginning, identified in the core from the sedimentary discordance recorded in the depth of 162 cm. In order to eliminate noise from the data series, the IP curve was smoothed with a moving average calculation of ten points. As can be seen in the graph of Figure 8, the concentration of IP in the sediments of the SGR follows the regional population growth curve (Fig. 8).

The sudden increase of IP and TP concentrations measured at ≈105 cm depth is consistent with a larger inflection of the curve that began in 1970. It should be noted, however, that this analysis should be done with caution since we do not have an accurate chronological assessment for the sediment accumulation rate for the study area.

4.4 Evaluation of anthropogenic influence

To evaluate the potential of anthropogenic influence on the concentrations of these elements, the IP concentrations along the sediment core are compared with the demographic growth curve of the Americana region from the time of reservoir filling (160 cm).

The sample resolution used in the IP analysis ranges from 2 to 4 cm and the mean deposition rate estimated for the core is 2.5 cm/year (Leite, 2002). Thus, to remove the influence of the interannual variability on the concentrations of these elements, a smoothing moving average curve of 10 points was calculated which, as a rough approximation, would represent an average of about 10 years.

In Figure 8 it is possible to point out that the growth rate of the IP concentrations is similar to the Americana city population growth curve. It suggests a link of the IP concentrations and the demographic and economic growth of the Metropolitan region of Campinas.

The influence of natural forcing, such as precipitation, on chemical aspects of SGR sediments was best observed using
five-points moving average curve for IP concentrations, which allowed to smooth the raw data series.

The moving average curve smooth part of the interannual and intra-seasonal variability once its signal can impair the comparison, especially in the case of this core that does not have a geochronological model. The smoothed IP curve is compared to the five-year series of rainfall anomalies measured in the SGR area (Fig. 9).

Variations in IP concentrations are in phase with the local rainfall oscillations estimated from the five-year mean of local rainfall anomalies. Thus, while the population growth curve seems to explain the trend of continuous increase of the contribution of IP in the reservoir, the variability of higher frequency, seems to be associated to interannual scale variations in the rainfall regime.

In this sense, we can assume that the variations of the nutrient supply in Salto Grande Reservoir are related to changes in the flow of rainwater in the Atibaia River drainage basin.

Tab. 1. Statistical description of phosphorus (P) results from the GSR sediment: total P (PT), organic P (PO) and inorganic P (PI).

<table>
<thead>
<tr>
<th>Variables</th>
<th>TP (μg/g)</th>
<th>OP (μg/g)</th>
<th>IP (μg/g)</th>
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<tbody>
<tr>
<td>Mean</td>
<td>1217</td>
<td>195</td>
<td>1022</td>
</tr>
<tr>
<td>Maximum</td>
<td>1512</td>
<td>346</td>
<td>1311</td>
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<tr>
<td>Minimum</td>
<td>848</td>
<td>11</td>
<td>731</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>167</td>
<td>80</td>
<td>162</td>
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<table>
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<th>Pre Reservoir</th>
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<tbody>
<tr>
<td>Mean</td>
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<td>158</td>
</tr>
<tr>
<td>Maximum</td>
<td>905</td>
<td>347</td>
</tr>
<tr>
<td>Minimum</td>
<td>204</td>
<td>60</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>272</td>
<td>104</td>
</tr>
</tbody>
</table>

Fig. 8. Comparison between the inorganic P (IP) concentration curve in the Salto Grande Reservoir and the population growth curve of the Americana city (IBGE, 2010), São Paulo. The light gray curve represents the raw data of IP and the curve in black the moving average series.
Fig. 9. Comparison of the demographic growth (IBGE, 2010), IP contents in the studied core (%) and precipitation (mm) trends.

5. Conclusion

The analyzed chemical markers of IP and OP showed a continuous and increasing influx of nutrients in the system, indicative of a progressive process of eutrophication of the Salto Grande Reservoir. There was also clearly coincident tendencies of the curves of demographic growth, precipitation and IP contents in the SGR, in such a way that the population growth curve seems to explain the tendency of continuous increase of the contribution of IP in the sedimentary column of the Salto Grande Reservoir. The variations of IP also have good relation with the variations, at a decadal scale, of the local precipitation. Variations of IP concentrations in the SGR sediments consistently follow the higher frequency variations of local precipitation, which suggests that the leaching of soils around the reservoir plays an important contribution for the P accumulated in the sediments of this reservoir.

Thus, the population growth curve seems to explain the trend of continuous increase of the contribution of IP in the reservoir and the variability of higher frequency, associated to the variations of the interannual scale due to more leaching of the surrounding soils during rainy periods. This may be conditioned to the use of fertilizers in the sugar cane crop traditionally grown on the northern flank of the reservoir.

Considering that the use of the soil around the reservoir, population growth and the variation of the precipitation rate exert a strong control of the IP input to the SGR, we can conclude that the higher values of IP recorded in the SGR result from the contribution of anthropogenic activities, which are triggering the eutrophication of this system.

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References


