

*Full Length Research Paper*

## Phosphorus fractionation in sediments of the ypacarai lake basin

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The aim of this paper was to determine the phosphorus fractions in the sediment, at different points of the tributaries, on the lake, and on the Ypacarai lake basin. There was a collection of 23 bottom sediment (SF) samples of 0 to 0.05 m of tributaries of the Ypacarai lake basin and 10 samples from the lake. The sand, silt and clay fractions and textural class were determined; in addition to the P forms, grouped in labile, moderately labile and nonlabile. The bottom sediments of the tributaries and of the lake presented scarce clay content, predominantly containing sand on the textural class. There is a greater amount of phosphorus in every evaluated fraction in the fine sediment of the tributaries than in the sediment of the lake. The greatest fractions of moderately labile phosphorus were obtained from the lake, presenting values considered to be adequate in the tributaries. However, in the tributaries, the determinations showed high variability between the points which run through densely populated regions, being that the three forms labile, moderately labile and nonlabile were found distributed in equal parts.

**Key words:** Available phosphorus, eutrophication, environmental contamination, erosion.

### INTRODUCTION

The state of the watercourses in densely populated regions suffers the effects of human activities in the watershed, with phosphorus as one of the key players for the eutrophication process of the water (Pellegrini, 2005). In rural areas, the application of high doses of P via inorganic mineral fertilizers or organic amendments leads to the saturation of the soil surface functional groups of

higher affinity (Rheinheimer, Anghinoni, 2003). In urban areas, the contamination is caused by the improper disposal of the organic material, such as sewage waste, industrial residues and household garbage, mainly from the use of detergents with polyphosphates. Based on the aforementioned studies of chemical elements fractionations, the sedimentary compartment applied to

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watercourses, are of utmost importance, recording the occurring processes in the aquatic ecosystem, serving as a great tool to understand the processes of the behaviour of phosphorus and other nutrients (Zhang et al., 2010).

The extraction of sedimentary phosphorus is grouped into five main fractions; it has been widely applied in soils, marine, lake and estuary sediments, and provides a more comprehensive analysis of the dynamic phosphorus than simply investigating the total phosphorus (Aquino, 2014). The labile P is the most important factor when the quality of the lake water is considered, as it is an essential nutrient for the occurrence of the eutrophication (Sharpley et al., 1987). The entry of the sediment in the body of water plays a fundamental role in P availability, it can work as source or drain of the element, the more the basin suffers the effects from men, the greater the entry of the sediment and of P in the particulate form (Schenatto, 2009). The quantity and the form of P found in the sediments vary widely among watercourses (Zhou et al., 2001) and the ability to release the P depends on the way it is adsorbed in its functional groups, specially on the silt and clay fractions (Zhu et al., 2013).

The organic P and the P connected to iron and aluminum oxy-hydroxides are the most abundant (Monbet et al., 2010), and the P connected to calcium is of lower availability (Kerr et al., 2011).

Once P is found in the water, there is a balance between the P fractionated in the solution and in the sediment, resulting into a quick balance on the surface of the particles; however, within its interior the balance is slow and the release of P can only occur when there is a resuspension of the particles found at the bottom of the water mass (Correl, 1999). In environments with low oxygen concentrations, there is an increase of P release due to the iron reduction and the surface of oxy-hydroxides are modified (Schenatto, 2009). In order to study the availability of P in the sediment, the study makes use of the P fractionation, which consists in performing successive extraction of the same sample of the sediment through different chemical extractors. In this context, the aim of this paper was to determine the phosphorus fractions in the sediment, in different points of the tributaries, in the lake, and the Ypacarai lake basin.

## MATERIALS AND METHODS

The Ypacarai lake is located to the East side of the city of Assunção (25° 19' 42,87" and 57° 20' 35,57" to 60 meters of altitude), with approximately 60 km<sup>2</sup>. The geological formation is composed of basic conglomerates and quartz crystals. There was a collection of 23 samples of bottom sediment (SF) of the tributaries of the lake basin and 10 samples of the sediment of the lake, coming to a total of 33 watershed points of the Ypacarailake (CHY) (Figure 1). At each point two samples were collected at a 0 to 05 m depth. The experiment was conducted in a completely randomized design, with 2 treatments, with samples of SF of the tributaries, with 23 repetitions and SF sample of the lake, with 10 repetitions. At each point there was a collection of two samples composed of various sub-samples, with two repetitions of laboratory, coming to a

total of 132 analyzed samples. The SF samples were dried in greenhouse at 50°C and sieved with a sieve of 63 µm to separate silt and clay from the sand fraction. The texture of the samples was determined through the volumetric pipette method (USDA, 1972).

The most commonly used methodology to perform the P fractionation is the one proposed by Hedley (Gatiboni et al., 2007), from which the P of the sediment can be grouped into labile, or P extracted through anion exchange resin and bicarbonate, or moderately labile, which is the P extracted through sodium hydroxide, and nonlabile which refers to the P extracted through strong acids (Rheinheimer et al., 2008). The samples of lime plus clay of the SF were used to determine the fractionation of P described by Hedley et al. (1982) with modifications proposed by Rheinheimer (2000). The forms of P were sequentially extracted through: Anion exchange resin (AMI 7001S) (P<sub>RIA</sub>); NaHCO<sub>3</sub> 0.5 mol L<sup>-1</sup> at pH 8,5 (P<sub>NaHCO3</sub>), NaOH 0.1 mol L<sup>-1</sup> (P<sub>NaOH01</sub>); HCl 1.0 mol L<sup>-1</sup>eNaOH 0.5 mol L<sup>-1</sup>(P<sub>NaOH0.5</sub>). All the extractors remained in contact with the samples for 16 h in agitator type "endover" 33 rpm followed by centrifugation at 2510 spin for 20 min. In the alkaline extracts of the solution of NaHCO<sub>3</sub> and NaOH, the available P was determined through the method from Dick and Tabatabai (1977), modified by He and Honeycutt (2005) and the total P performing the extraction through digestion with ammonium persulfate and H<sub>2</sub>SO<sub>4</sub> in autoclave at 121°C and subsequently determined by Murphy and Riley (1962).

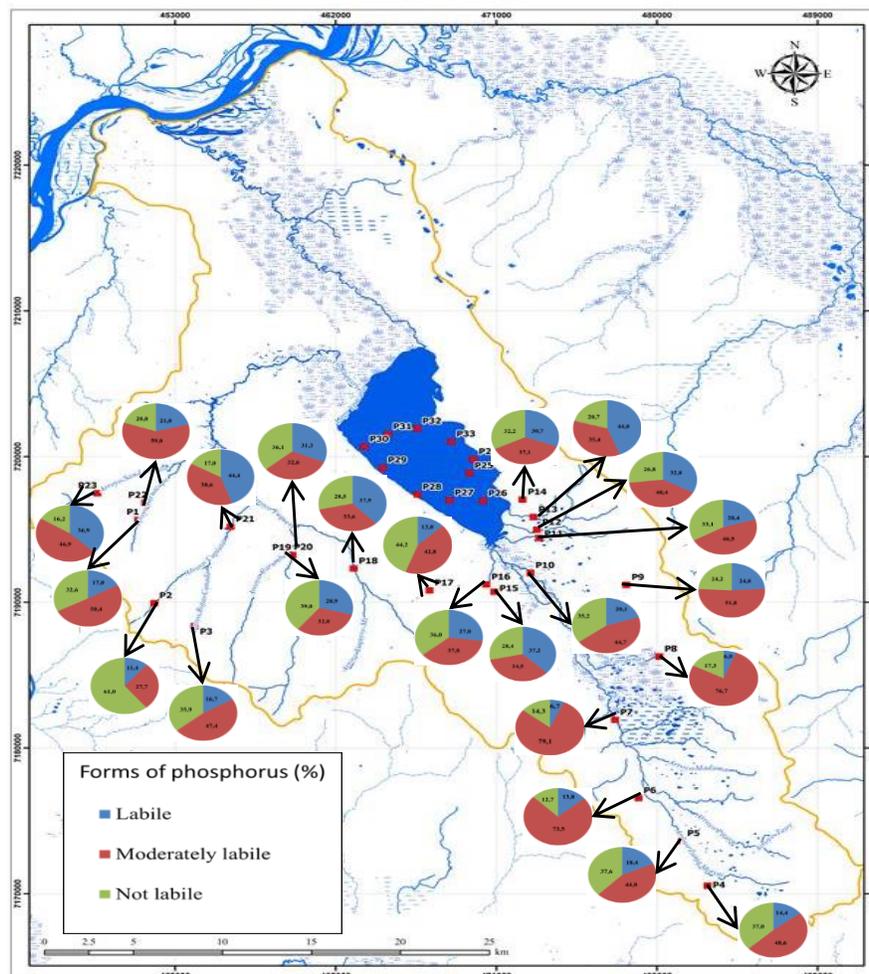
Afterwards, the residue was dried, ground and had the residual P extracted by the method H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + MgCl<sub>2</sub> (Olsen and Sommers, 1982). The P determinations extracted were estimated by the method of Murphy and Riley (1962). The inorganic P forms extracted through the RTA and through NaHCO<sub>3</sub> were considered "labile" forms. The P extracted through the NaOH was considered a "moderately labile" form. The P extracted through HCl and the residual inorganic P were considered little labile and nonlabile, respectively. The total P was estimated by the sum of all extractions. The statistical analysis was performed by the statistical software Assisat (Silva and Azevedo, 2009). The obtained data were submitted to a variance analysis. In this finding, significant effect on the averages were submitted to the Tukey test at 5% of probability.

## RESULTS AND DISCUSSION

From all the analyzed samples, corresponding to the tributaries from the Ypacarai Lake, numbered from P1 to P23, (Figure 1) 91% of them presented sandy textural class, with high sand content which ranged from 92.2 to 94.9% and low clay percentages of only 0.3 to 1%. The remaining samples 9% had loamy sand texture. In the samples collected at the Ypacarai Lake, corresponding from P24 to P33, the clay content was greater, ranging from 6 to 15%. The adsorption capacity of P is inversely related to the size of the particles, whose bioavailability is difficult to determine, because of its high affinity with the lost particles (sediments) and the reversibility of the adsorption/desorption process (Zhu et al., 2013). The way in which the adsorbed P is released, will depend on the physical-chemical conditions of the water interface on the soil and on how P is connected to particles of the sediment (Pettersson and Istvanovics, 1988).

On average, the different P forms were greater in the sediment of tributaries on the lake (Table 1). The P resin is extracted twice in SF on tributaries and SF of the lake, considering that this one is the most available and can be

Map of relative percentage of phosphorus  
in the Ypacarai Lake basin



**Figure 1.** Relative percentage of the labile, moderately labile and nonlabile phosphorus forms, in the bottom sediment of the tributaries, obtained by phosphorus fractionation in the watershed of the Ypacarailake, Paraguay. Red: moderately labile; green: nonlabile; blue: labile.

**Table 1.** Phosphorus forms in the bottom sediment of the tributaries and the lake, obtained by phosphorus fractionation in the watershed of the Ypacarailake, Paraguay.

Site	Phosphorus fractionation								Residual P	Total P
	Resi	NaHCO <sub>3</sub>		NaOH 0.1 M		HCl 1 M	NaOH 0.5 M			
	Pi	Pi	Po	Pi	Po	Pi	Pi	Po		
	mg kg <sup>-1</sup>									
Tributaris	7 <sup>a</sup>	33 <sup>a</sup>	135 <sup>a</sup>	54 <sup>a</sup>	103 <sup>a</sup>	113 <sup>a</sup>	156 <sup>a</sup>	29 <sup>a</sup>	90 <sup>a</sup>	692 <sup>a</sup>
Lake	3 <sup>b</sup>	8 <sup>b</sup>	22 <sup>b</sup>	34 <sup>b</sup>	54 <sup>b</sup>	10 <sup>b</sup>	31 <sup>b</sup>	18 <sup>b</sup>	56 <sup>b</sup>	219 <sup>b</sup>
CV	16.6	17.2	31.2	42.5	43.9	31.2	17.4	56.5	65.4	19.4

<sup>1</sup>Means followed by the same letter in are not significantly different (Tukey > 0.05). Pi = inorganic phosphorus; Po = organic phosphorus.

easily used by aquatic organisms due to its availability. The NaHCO<sub>3</sub>, both in the biological (Po) and inorganic (Pi) form is from 4 to 6 times, respectively, on the

tributaries of the lake SF. Phosphorus extracted through bicarbonate can usually become available for the organisms, which occurs when there are environments

where there is pH variation, redox or reduction of P content soluble in water (Schenatto, 2009). NaOH 0.1 M and NaOH 0.5 M, represent P which is connected mainly to iron and aluminum oxy-hydroxide, in addition to being on the organic matter, if water enters on the course of some organic matter from water erosion or decomposing organic materials, there is availability of this P (Schenatto, 2009; Monbet et al., 2010).

However, under conditions with low or zero oxygen concentration, there is release of P connected to the iron, due to the reduction of this element and the surface of the oxy-hydroxides is modified, releasing P (Vahl, 1999; Rannotodos, 2007). A large part of P is on the biological form and can represent up to 25% of P potentially bioavailable when they are mineralized (Correl, 1999; Bhadha and Jawitz, 2010). The P extracted through hydrochloric acid (HCl) (P-HCL), as well as other P forms, make is in past tense greater on the SF of tributaries, eleven times higher than on the SF of the lake. Usually, the amount of P-HCl present in lake sediments is below the water resources, especially in areas where acidic soils are found, because the extracted P-HCl is connected to the calcium of minerals, such as calcite, apatites or neof ormation of calcium phosphate of Pi. As it is important on alkaline soils, or in rural areas where phosphate fertilizers is applied in the form of natural phosphate, or when there is the application of high doses of agricultural limestone, which allows the neof ormation of calcium phosphate (Gatiboni et al., 2007), which is not observed on the basin under study.

There is on average three times the P total on the SF of tributaries  $692 \text{ mg kg}^{-1}$  than on the lake  $219 \text{ mg kg}^{-1}$  which is a concern, considering that the sediment will end up deposited on the lake and that currently presents problems due to the eutrophication of its waters; if corrective measures are not taken on the Ypacarai lake to prevent the entry of sediments rich in P into the lake, these problems will get worse. Previously, Ritterbusch (1988), in a limnological study of the Ypacarai Lake, found high concentrations of nitrogen and phosphorus available, especially P, significantly exceeding  $30 \text{ mg L}^{-1}$ , which is considered the limit for the eutrophication process.

The same author observed that the total P is larger on the outputs of the system that is being retained on the lake bed, and a very high level of total P in areas influenced by domestic and industrial sewage in the districts of Areguá and San Bernardino. In studies in southern Brazil, on sampling carried out on rivers that are part of the Mirim lake basin in RS, contents above the level of  $0.1 \text{ mg L}^{-1}$  (Coradi et al., 2009) were observed. Diel et al. (2007) found that, on average, the content of total P in the water destined for rice irrigation was of  $0,041 \text{ mg L}^{-1}$ , while in dams, ponds and rivers the average values of P were 0,027; 0,035;  $0,060 \text{ mg L}^{-1}$ . When the samples of SF tributaries are compared, a lot of variation is noted on the total P value (Figure 2), with

a higher total amount of P on the sample of SF collected in the (P23) flow and the San Lorenzo flow Tayuazape (P1, P22), which runs to the same water flow. These points are located in streams with high anthropic occupation, so that the high levels of total P can be found through removal of domestic and industrial waste. In addition, the P16, P17, and P18 points which crosses the cities of Ypacarai and Itaugua have high levels of total P, although, almost half of the total P, when compared to the tributaries run through San Lorenzo.

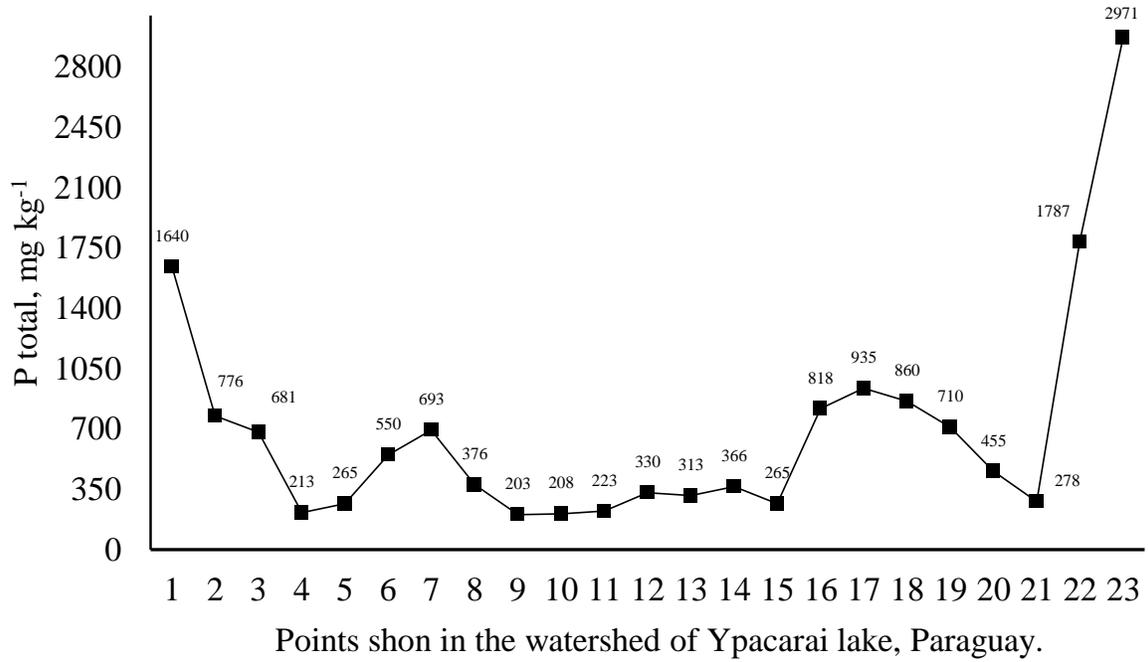
The tributaries located on the South of the basin, from Arroyo ZanjaMoroti (P4, P5, and P6 points), which has its source in the Paraguari district and disgorges in the Pirayú (P7) stream, until its mouth in Ypacarai lake and tributaries located to the East side of the Ypacarai lake, which has two headsprings in the districts of Caacupé (P8), Ypacarai (P9 and P10) and San Bernardino (P11, P12, P13 and P14) usually has low levels of total P (Figure 2). These watershed areas are sparsely populated, so the entries of P would come from the pollution from diffuse sources, as agriculture and livestock that takes place in a large part of the basin (Figure 3). The results obtained at the Capiatá stream can be highlighted, alongside the headspring (P2 and P3) possessing relatively high amounts of P ( $776$  and  $681 \text{ mg kg}^{-1}$ ). However, at P21 point there is less, with 50% of total P on the header  $278 \text{ mg kg}^{-1}$ , so it would be advisable to carry out a new SF sampling, to check if there was any collection of error or if there actually is any factor that allows total reduction of P content, as gallery forests and marshes. On average, to the south of the Ypacarai Lake there is a lower P total than the SF of the tributaries (Table 1); however, at different points of comparison sampling Ypacarai Lake shows that there is a variation in total amount of P at its SF, and to the south of the lake it is more than total P, especially at the nearest point to the city of Ypacarai (P26), which presented  $356 \text{ mg kg}^{-1}$ . In the middle of the lake there is less total P, especially at the shores located in the Areguá district (P30, P29, P31 and P32).

## Conclusion

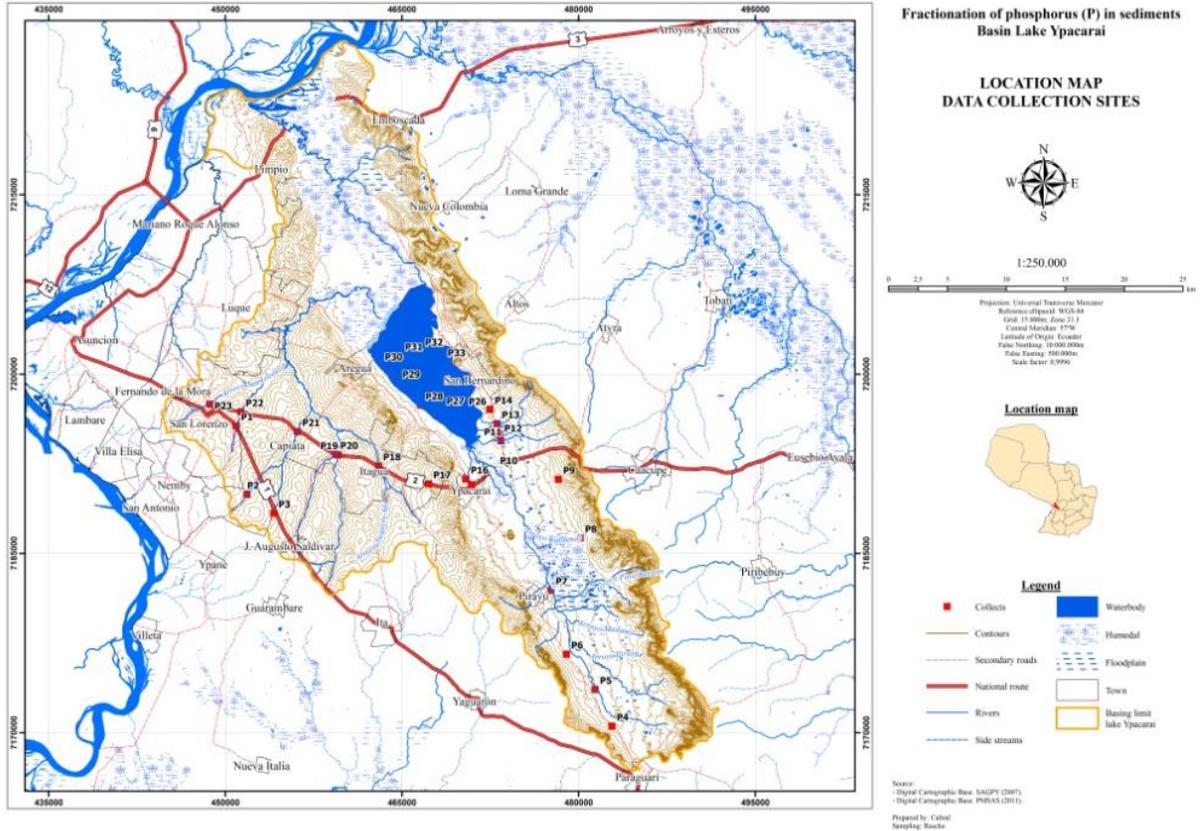
The concentration of populations and anthropogenic activities in the shores of the Ypacaraylake, the available P in the lake sediments increased up to 0.05 m deep. The saturation of the absorption sites of P in the lake sediments; evaluated by the determination of the labile, moderately labile and nonlabile forms, presented variability, being higher in the lake than in the tributaries. Eutrophication is found both in the lake as in the tributaries in all the evaluated points.

## Conflict of Interests

The authors have not declared any conflict of interests.



**Figure 2.** Total phosphorus in the bottom sediment of the tributaries obtained by the sum of fractions on the watershed of Ypacarailake, Paraguay.



**Figure 3.** Geographical distribution of the collection points of the bottom sediment of the tributaries and the Ypacarai lake, in the watershed of the Ypacarailake, Paraguay.

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