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Hipolimnion water quality and its relationship to internal P loading in an eutrophicated water body: San Roque Reservoir (Córdoba, Argentina)

La qualité de l'eau de l'hipolimnion et son rapport avec le chargement interne de P dans l'eutrophisation de la masse d'eau : Réservoir De San Roque (Córdoba, L'Argentine)

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ABSTRACT

San Roque Reservoir (Córdoba, Argentina) is the main resource for drinking water to the city of Córdoba and its surroundings with a total population of nearly 1.5 million inhabitants. Water-quality related problems have increased in the reservoir due to deforestation, urban run-off and particularly the discharge of untreated sewage. The reservoir is currently receiving large inflows of nutrients and the process of eutrophication started decades ago. As a consequence, regular and continuous algae blooms occurred since 1988. The reservoir presents summertime stratification regime, when thermocline is formed, and consequently the bottom layer becomes anoxic. Redox potential gets reductive and numerous compounds release from sediment such as phosphorus. This work presents the results of a comprehensive field study consisting of 12 campaigns during a chronological year (2000). Water at the hipolimnion and sediment samples were taken at three monitoring stations: the center of the reservoir, old wall and the water intake surroundings. *In situ* dissolved oxygen and temperature were measured in the water column. Phosphorus fractions and related phosphorus ions were analyzed in water samples while total phosphorus was determined in sediment samples. The gathered information reveals the clear influence of anoxic conditions in the dynamics of phosphorus processes related to ion sediment release.

RÉSUMÉ

Le réservoir de San Roque (Córdoba, Argentine) est la ressource principale d'eau potable de la ville de Córdoba et de son environnement avec une population totale de presque 1.5 million d'habitants. Les problèmes liés à la qualité de l'eau ont augmenté dans le réservoir suite au déboisement, à l'écoulement urbain et en particulier à la décharge des eaux d'égout non traitées. Le réservoir reçoit actuellement de grands apports nutritifs et le processus d'eutrophisation a commencé depuis des décennies. Par suite, les poussées phytoplantoniques se sont produites de façon régulière et continue depuis 1988. Le réservoir se stratifie l'été, quand se forme la thermocline, et par conséquent la couche inférieure devient anoxique. Le potentiel redox devient réducteur et de nombreux composés se libèrent du sédiment tel que le phosphore. Ce travail présente les résultats d'une étude complète sur le terrain composée de 12 campagnes pendant une année (2000).L'eau des échantillons de l'hipolimnion et des sédiments a été prise à trois stations de contrôle : au centre du réservoir, au vieux mur et au voisinage de la prise d'eau. L'oxygène dissous et la température in situ ont été mesurés dans la colonne d'eau. Des fractions de phosphore et les ions relatifs au phosphore ont été analysés dans des échantillons d'eau tandis que le phosphore total était déterminé dans des échantillons de sédiment. L'information recueillie montre clairement l'influence des conditions anoxiques dans la dynamique des processus du phosphore liés au dégagement d'ion des sédiment.

Keywords: Eutrophication, internal load, P cycle.

1 Introduction

Nowadays lakes and reservoirs are suffering from the process of eutrophication—nutrient enrichment—and water quality has been deteriorating during latter decades worldwide. Eutrophication control has been strongly focused in external nutrient load (mainly phosphorus, as it acts as limiting nutrient) from point and diffuse sources and, on the other hand, internal loading control has been rarely explored. Bottom sediments provide the necessary phosphorus to sustain large biomass in water bodies. Particles and phosphorus could be released from benthos through physical, chemical or biological disturbances and processes (Holdren and Armstrong, 1980). The physicochemical characteristics of the sediments vary seasonally and produce the absorption

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and desorption phenomena. The release of components from the sediments are influenced by its own transformations together with its structure. The underneath fraction of the sediments is practically isolated from the hydro-mechanisms of the bottom water layer and the sediment traps some components in a definite way. Water quality factors such as intensity of thermal stratification, dissolved oxygen conditions and pH influence the uptake and release of phosphorus rates. This release happens to be highly correlated to manganese and iron manganese concentrations. Another significant role is played by the geographic location and morphometry characteristics (Margalef, 1983).

Monomictic reservoirs are located in template climate in the center countryside of Argentina and undergo thermal stratification during summertime, thus hipolimnion layer may get anoxic and chemical changes occur. The general objective of this paper is to explain these changes in sediment components release in San Roque Reservoir, Córdoba, Argentina. In particular, the aim is to describe the phosphorus metabolism and its relationship to manganese and iron behavior.

2 Study area

San Roque Reservoir (31°22′56″ S, 64°27′56″ W) is located in the Punilla Valley, Cordoba, Argentina, at 600 m above sea level. It belongs to the high Suquía Basin and its drainage area has a surface of 1750 km^2. It has four tributaries (Cosquín River, San Antonio River, Las Mojarras Stream and Los Chorrillos Stream) and one outlet, Suquía River. The climate of the area is described as semi-arid as the basin is characterized by summer precipitation (85% of the total annual rainfall). Even though the annual mean rainfall in the basin is 700 mm, there had been some wet years when precipitation reached up to 1100 mm and some dry years with no more rain than 400 mm. Intense solar radiation derives in high evaporation. San Roque Reservoir used to have a capacity of 201 hm^3 and today it is reduced to 190 due to siltation. Figure 1 shows the reservoir aerial view, the tributaries location (1, Cosquín River; 2, Los Chorrillos Stream; 3, Las Mojarras Stream; 4, San Antonio River) and the selected sampling sites (5, Center; 6, Old Wall; 7, Water Intake). Number 8 represents the outlet (Suquía River). Nowadays, the reservoir is used to prevent floods, to provide drinking water, produce electrical power, minor irrigation, recreation and tourism. Main hydraulic characteristics of the reservoir are summarized in Table 1. A hydraulic characteristic of this reservoir is the presence of a submerged wall, which was the original dam and replaced for the actual one in 1944 (Granero *et al.*, 2001), located approximately 100 m away from it. An important feature to mention is that the water intake, which provides water to the treatment plants, is located between the two walls, at 13 m from the bottom. The water is conveyed in pressurized channels to the water plants after passing through the hydroelectric plant. As for the reservoir trophic status, it is known to be eutrophic and the limiting nutrient is phosphorus (Bustamante *et al.*, 2000).

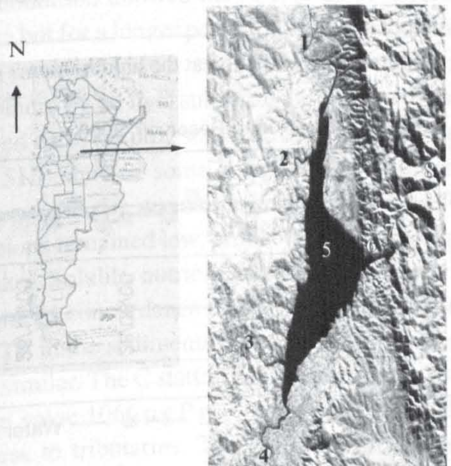

Figure 1 Area view of San Roque reservoir.

Table 1 The main characteristics of San Roque Reservoir

Geographical position	31°22′56″ S 64°27′56″ W
Drainage area	1750 km^2
Dam type	Concrete; curve plant
Surface	15.01 km^2
Volume	201 hm^3
Maximum depth at spillway	35.30 m
Mean depth	13 m
Water level	Regulated
Level annual fluctuation	6 m
Residence time	0.1–0.7 years
Tributaries (mean annual flux)	
San Antonio River	2.7 m^3 sg^{-1}
Cosquín River	4.4 m^3 sg^{-1}
Las Mojarras Stream	0.5 m^3 sg^{-1}
Los Chorrillos Stream	0.7 m^3 sg^{-1}
Outlet: Suquía River	9.6 m^3 sg^{-1}
Uses	Drinking water, hydroelectricity supply, recreation and tourism

The sediment of San Roque reservoir is characterized by 52.5% of lime, 38.5% of clay and 9% of sand, the mean sedimentation rate is 0.286 hm^3 year^{-1} (Santa and Herrero Machado, 1979) and density is 1169.1 kg m^{-3} (Ambrosino, 1987). In the basin the volume of sediments have been quantified in two subbasins, the northern one, which corresponds to Cosquín River and Las Mojarras Stream, and the southern one, San Antonio River and Los Chorrillos Stream. Therefore, the two big areas are considered to be the total drainage basin (Fernández, 1998). San Antonio river and Los Chorrillos stream sub-basins have a specific weight of 1159.6 kg m^{-3} and a volume of 7.4 hm^3. Its specific degradation is 250.3 Tn km^2 year^{-1}. Cosquín river and Las Mojarras stream information are 1172.5 kg m^{-3}, 6.1 hm^3 and 147.4 Tn km^2 year^{-1}, respectively.

3 Methodology

The selected monitoring stations were the Center, Old Wall and Water Intake (Fig. 1). Vertical profiles of dissolved oxygen (DO) (mg l^{-1}), temperature (T) (°C), pH and redox potential (ORP) (mV) were recorded with Multiparametric Horiba U-23 Probe. Transparency was obtained by Secchi disk. Water samples were extracted with Van Dorn bottle at the hipolimnion, 1 m above the bottom layer. According to the Standard Methods (APHA, 1992) total phosphorus (TP) ($\mu g\,P\,l^{-1}$) was analyzed by persulfate digestion and soluble reactive phosphorus (SRP) ($\mu g\,P\,l^{-1}$) by ascorbic acid method. Ions manganese (Mn) ($mg\,Mn\,l^{-1}$) and iron (Fe) ($mg\,Fe\,l^{-1}$) were determined by flame atomic absorption.

Sediment samples were extracted with Eckman type dredge. Total phosphorus (TP) ($\mu g\,P\,g^{-1}$) of dry sediment was obtained by ignition method and acid hydrolysis and the reactive phosphorus by the ascorbic acid method. Fractionation of P was held by the analytical process suggested by Psneer and Pucsko (1988). It consists of four extraction steps: (a) NH_4Cl—for thermal labile P; (b) ditionite—P adsorbed to iron hydroxide surfaces; (c) NaOH—P adsorbed to metal oxides; and (d) HCl—P bound to carbonate. Release rates were calculated by measuring the PRS in contact sediment water, changing pH and DO conditions.

4 Results and discussion

As can be observed from Fig. 2, stratification was evident during summertime at all stations and the temperature gradient remained stable until middle fall when the mixing process occurred and the temperature was similar at all depths in the water column. At the beginning of the fall, solar radiation started to rise. Then, stratification process dawned again (monomictic lake). The difference in density from surface to the bottom layer allows DO depletion. The physical barrier produced by the thermocline prevents DO diffusion to lower layers. Therefore, DO concentrations of hipolimnion were consumed by microorganisms, reaching to null values at the bottom layer. The mixing period restores DO conditions and the hipolimnion continued oxygenated the rest of the year.

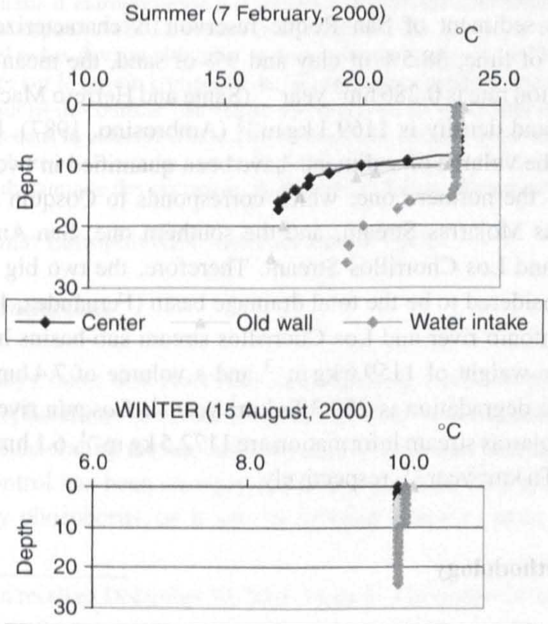

Figure 2 T and DO at three stations during winter and summertime.

Figure 3 shows the pH evolution at the hipolimnion during the different months of the year. It can clearly be seen that during summertime, pH went down to 6.5 and this value allows not only the absorption of P but also its release, making the interchange very dynamic. The decrease of pH is directly related to the DO depletion, producing less OH^- ions. This condition can be simply explained by the fact as DO got consumed, OH^- ions got into H^+ ions, and the pH obviously dropped. The decrease of pH aids other chemical reactions which developed adverse effects in the water quality at the hipolimnion. As OH^- ions decreased, the ORP in the vertical gradient suffered modifications which turned it to negative values, settling reductive properties (Fig. 4). According to Margalef (1983), redox potential in the hipolimnion and in the sediment water–interface governs oxidation number of sediment components. If an element diffuses and migrates through the sediment its state of oxidation may be affected and even it may precipitate. The solid structure of the sediment traps the component and later on it gets dissolved and freely released to the water. An example of this behavior are Fe and Mn ions. Mortimer (1949) demonstrated that when ORP drops Fe, Mn and P get released. The results obtained in San Roque Reservoir show this mentioned evolution with similar performance at the three stations (Fig. 5). When the hipolimnion was anoxic and consequently reductive, Fe and Mn released from the sediments and they got lightly absorbed. The time reaction as well as the rates of absorption–desortion are due to pH. In San Roque Reservoir, Fe and Mn release rates exceeded absorption rates and their concentrations in the hipolimnion rose. The restoration of DO conditions in the mixing period caused the oxidation of ferrous ion and the

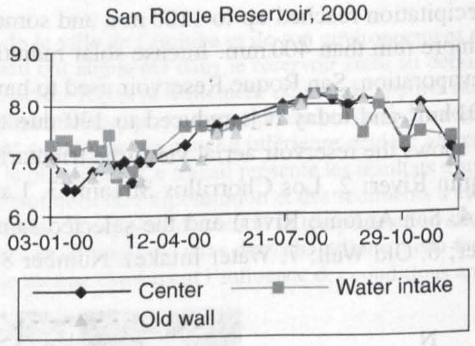

Figure 3 pH evolution at the hipolimnion.

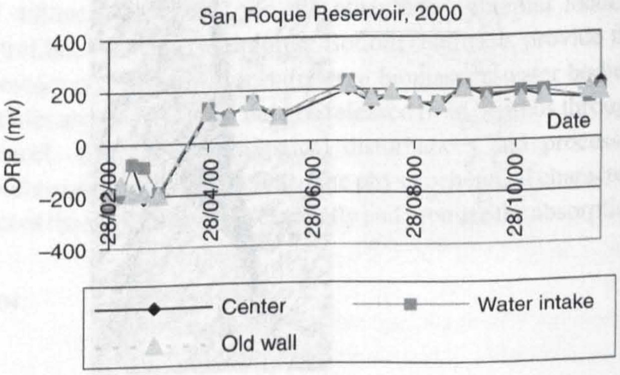

Figure 4 ORP evolution in the hipolimnion.

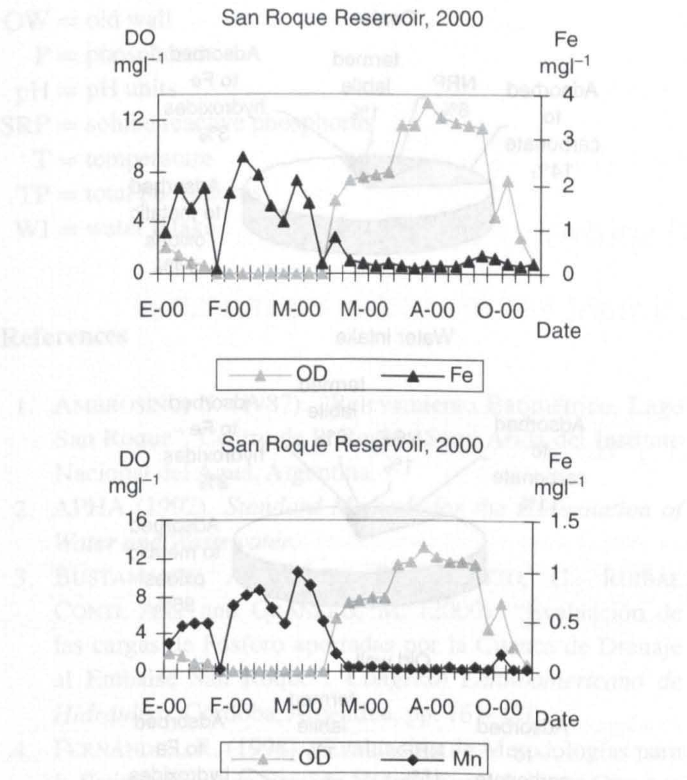

Figure 5 Bivalent cations evolution at the hipolimnion.

simultaneous reduction of phosphate as ferric phosphate. Manganese is oxidized with a lower rate but it definitely precipitated during the mixing period. A part of particulate ferric phosphate may be slowly hydrolyzed and then dissolved in the water but most of it is back in the bottom by sedimentation (Wetzel, 1983). It can be inferred from all this that the dynamics of Fe and Mn is the key in phosphorus internal exchange. Thus, as their concentrations rise at the hipolimnion, P release should be strongly considered.

Despite the evident increase of this nutrient in the whole hipolimnion (Fig. 6), the C location showed the highest peak of 420 μg P l^{-1} in February. The C station is located in a relative shallow part (mean depth of 15 m) compared to the OW station (22 m) and the WI station (26 m). As a result of thermal stratification and its depth, the C became anoxic before OW and WI did. This condition allowed the release of TP with similar desorption rate but for a longer period of time. On the other hand, the WI station recorded lowest values of P. This station is separated from the others by an hydraulic structure, the old wall. It acts as a submerged dam, keeping sediments and organic material away. Although SRP showed some peaks during summertime in the three stations, the rise was not as much evident as TP. The SRP concentrations remained low, probably as a result of phytoplankton's uptake. Soluble nutrient fractions became scarce during summertime in concordance to the increased growing biomass. Values of TP in the sediments during the four seasons happened to be very similar. The C station has a concentration of TP recording a mean value 1066 μg P g^{-1} of dry sediment and it is due to its closeness to tributaries. The WI station has less amount of sediment due to the presence of the old submerged dam which disables the regular sediment transport from the reservoir to the spillway area. In addition, TP in the sediment is lower than in the C with a mean concentration of 738 μg P g^{-1} of dry sediment. As for the OW station, it recorded a mean concentration of 1222 μg P g^{-1} (Fig. 7).

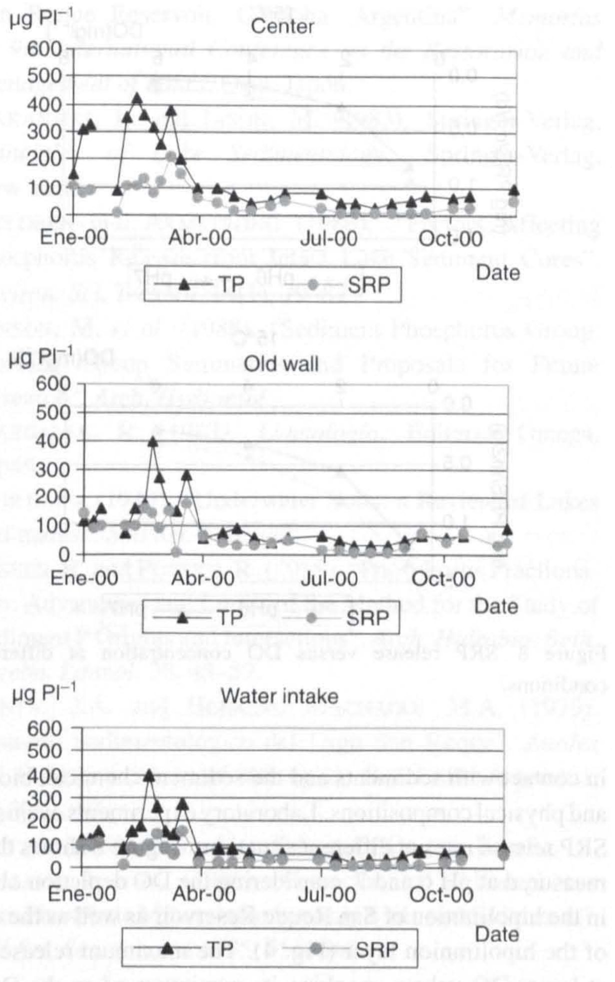

Figure 6 Phosphorus evolution at the hipolimnion.

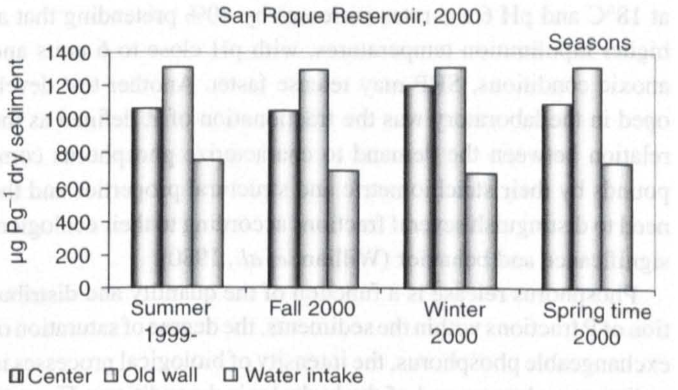

Figure 7 Seasonal variation of TP in the sediment.

Aside from resuspension, the release of P from reservoir bottom sediment involves the mobilization from particulate to dissolved form followed by transportation into the water column (Hakanson and Jason, 1983). Phosphorus release is primarily defined by the net flux of P from sediment to lake water which occurs when solubilization and upwards transport exceed phosphorus fixation in sediments (Janson *et al.*, 1988). This mechanism is due to the pH, temperature and DO conditions in the water

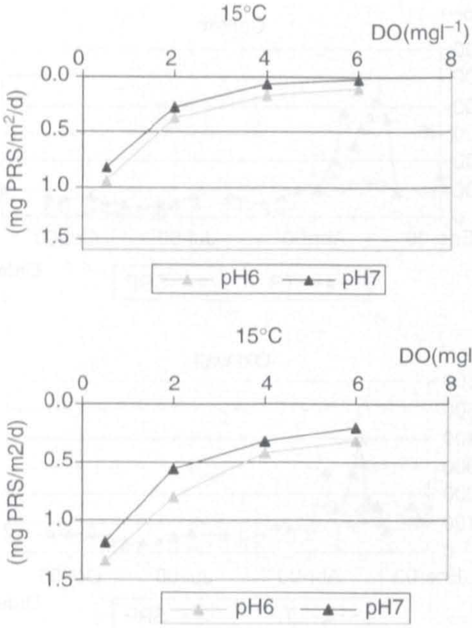

Figure 8 SRP release versus DO concentration at different pH conditions.

in contact with sediments and the sediment chemical, biological and physical compositions. Laboratory experiments evaluated the SRP release rates at different situations. Figure 8 shows the rates measured at pH 6 and 7, considering the DO depletion observed in the hipolimnion of San Roque Reservoir as well as the density of the hipolimnion layer (Fig. 4). The maximum release rate is at lower DO values, reaching its maximum when the DO concentration is zero at both experimental temperatures. However, at 18°C and pH 6 the rates increases by 40% pretending that at higher hipolimnion temperatures, with pH close to 6 units and anoxic conditions, SRP may release faster. Another test developed in the laboratory was the fractionation of P, defined as the relation between the demand to characterize phosphorus compounds by their steichiometric and structural properties and the need to distinguish several fractions according to their ecological significance and behavior (William *et al.*, 1980).

Phosphorus release is a function of the quantity and distribution of P fractions within the sediments, the degree of saturation of exchangeable phosphorus, the intensity of biological processes in sediment and water and of the hydrological conditions. Figure 9 shows the percentages of the extracted P fractions from the sediment of San Roque Reservoir. Fractionation of P allows the differentiation of these forms, relevant environmental parameters including pH, redox potential and temperature interacts in the mobilization of P and the transport processes include diffusion, turbulence, and bioturbation. The three stations recorded low ($<1\%$) concentration of thermal labile P, 2–3% of P adsorbed to iron hydroxide and 11–15% of P adsorbed to carbonates. The main differences found between the three stations were the fraction of P adsorbed to metallic oxides and the non-reactive phosphorus (NRP) defined as the difference of total phosphorus and the total of the reactive fractions. WI station showed the highest percentage of P adsorbed to Al_2O_3 and other surfaces, exchangeable against OH^- and P compounds soluble in basis.

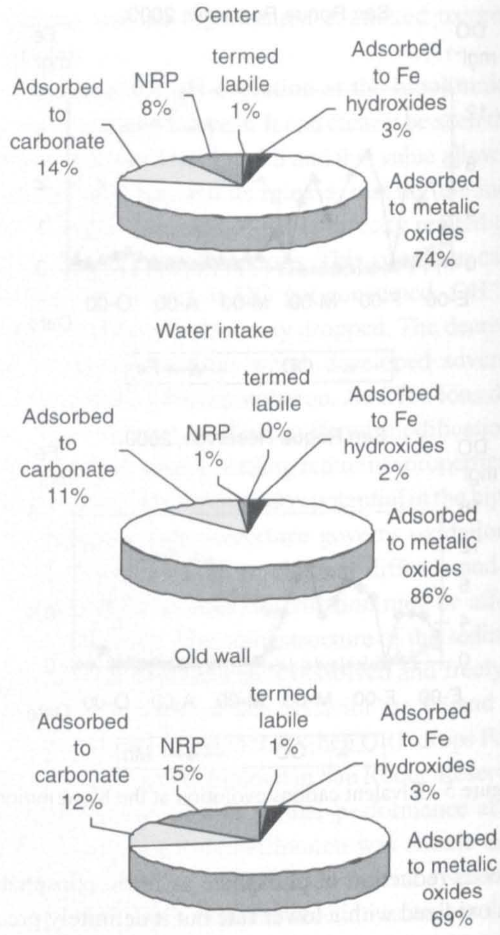

Figure 9 Fractionation of P in the sediment of San Roque Reservoir.

C and OW stations have this fraction as the major one. OW happened to have the highest percentage of NRP. As this is the station with higher amount of sediment, P may have trapped definitely together with Mn, Fe and other components

5 Conclusions

Sediments play a very important role in the eutrophication process in San Roque Reservoir acting as a nutrient storage component. Water at the hipolimnion depends not only on the water quality of above layers but also on the sediment water interface. Thus, nutrients and other components get released from the sediments. It is relevant for decision-makers to put efforts in the estimation of internal loads of nutrients in order to achieve a successful reservoir management. Internal P load should be use as a remediation tool.

Notation

C = center
DO = dissolved oxygen
Fe = iron
Mn = manganese
NRP = non-reactive phosphorus
ORP = redox potential

OW = old wall
P = phosphorus
pH = pH units
SRP = solube reactive phosphorus
T = temperature
TP = total phosphorus
WI = water intake

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